JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

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1916. Vol. CIX. Part II., pp. 649–end.

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C.
1916.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BRUNSWICK ST., STAMFORD ST., S.E.,
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assistance of the organic chemist. We want next to trace the intermediate stages of the reactions which intervene in the conversion of the amino-acid into a new type of structure. I would like, indeed, to feel that the few facts and the more numerous suggestions which have been before you this evening—facts and suggestions won in a very narrow field of research—may suffice to leave behind the impression in your mind that, because intermediary metabolism deals so largely with materials of which the actual molecular structure is known or ascertainable, the trained thought of the organic chemist has abundant opportunities in connexion with physiological research. We have dealt with protein metabolism alone, but it is equally true of metabolism in all its aspects. You may urge, of course, that the formation of the tissue complexes with their extreme chemical elusiveness is, after all, the most significant step in metabolism; so in a sense it is. The physical and physico-chemical properties of these complexes confer on the living cell its prominent mechano-motor properties and many of its reactivities, as well as providing the milieu in which chemical reactions occur. In my own belief, however, these complexes, once formed, are, in the chemical sense, essentially stable in all but one particular. Just as they are formed and maintained by the condensation (in the technical sense of the word) of the simpler molecules which are ever circulating in the blood, so are they liable to hydrolytic disintegration, yielding, like the food, simple materials for fresh synthesis or materials to undergo oxidation and provide energy to the body. Condensation and hydrolysis respectively lock and unlock the door which prevents or permits the occurrence of those oxidations and that regrouping of units which form the essential chapter in the chemical dynamics of metabolism. On the other side of that door there is relative chemical stability. About the details of condensation and hydrolysis in the tissues we have an indefinite amount to learn, but in connexion with large aspects of metabolism they may be taken for granted. If we follow our molecules of known structure up to the door, and follow them yet again as they emerge from it, we shall learn a large part of what we want to know about the chemical dynamics of the animal body.

LIV.—*The Isomerism of the Oximes. Part VIII. Carbanilino- and Carbethoxy-derivatives of the Oximes and the Mechanism of Isomeric Change in the Oximes and their Derivatives.*

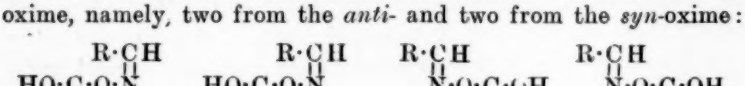
By Oscar Lisle Brady and Frederick Percy Dunn.

In a previous communication (T., 1913, **103**, 1613) it has been mentioned that Goldschmidt and van Rietschoten (*Ber.*, 1893, **26**, 2087) have obtained what they considered to be three isomeric carbanilino-*m*-nitrobenzaldoximes, two derived from the *anti*-oxime melting at 105° (I) and 139° (II) respectively and one derived from the *syn*-oxime melting at 75° (III). The substance (I) was obtained by the action of phenylcarbimide on *m*-nitrobenz*anti*-aldoxime in ethereal solution, the compounds being allowed to interact for only twenty-four hours. If the reaction mixture is left for a longer time the compound (II) is obtained; the compound (II) is also the product if compound (I) is boiled for a short time with alcohol or benzene.

The Hantzsch-Werner hypothesis, which Goldschmidt and van Rietschoten were supporting, failed to account for the existence of these three isomerides, and it was suggested that the new compound might be accounted for by *cis-trans*-isomerism on the second nitrogen atom thus:

Similarly, three carbanilino-derivatives had been obtained from benzaldoxime, but in this case it was the *syn*-oxime that gave two compounds.

If the views of Goldschmidt and van Rietschoten were correct, there should be four carbanilino-derivatives obtainable from each oxime, namely, two from the *anti*- and two from the *syn*-oxime:



From the *anti*-oxime. From the *syn*-oxime.

There is, however, no evidence of the existence of a fourth isomeride. Further, if this theory is accepted, other carbanilino-derivatives should exist in two forms.

During the investigation of the hydroxybenzaldoximes, the

present authors prepared the *o*-, *m*-, and *p*-carbanilino-oxybenzaldehydes, and it was thought that these compounds might behave similarly to carbanilino-*m*-nitrobenzaldoxime if boiled with alcohol. It was found, however, that such treatment resulted in their decomposition into hydroxybenzaldehyde, aniline, and diphenylcarbamide. This result led to the investigation of the compound (II) obtained by Goldschmidt by boiling compound (I) with alcohol, as it was possible that this was a mixture. This was, to a certain extent, found to be the case, as the compound obtained by following Goldschmidt's method and melting at 139—140° was found to contain traces of diphenylcarbamide and *m*-nitrobenzonitrile, and after careful purification melted at 148°.

A more fruitful observation was that the carbanilino-*syn*-aldoximes, on keeping for a few days, undergo decomposition with the formation of aniline, diphenylcarbamide, the corresponding nitrile, and carbanilino-*anti*-aldoxime, a fact which seems to have been overlooked by other observers.

Carbanilino-*m*-nitrobenzaldoxime has been prepared according to Goldschmidt's method. In every experiment performed, the substance obtained at the end of twenty-four hours was found to melt in the neighbourhood of 105°; recrystallisation from cold solvents did not affect the melting point to any great extent, but repeated recrystallisation from hot alcohol gradually raised it to 148°. If the compound is boiled for one hour with alcohol and the solution cooled, the substance separating melts at 138°, and on recrystallisation at 148°. It was found, however, that the compound melting at 105°, on keeping for a few days, decomposed, and from the decomposition products there were obtained aniline, diphenylcarbamide, *m*-nitrobenzonitrile, and carbanilino-*m*-nitrobenz*anti*-aldoxime. This behaviour, characteristic of the carbanilino*syn*-aldoximes, suggested that compound (I) might be a mixture of compounds (II) and (III). It was found that this was the case, there being present, in addition, a small quantity of diphenylcarbamide and *m*-nitrobenzaldoxime. This explanation has probably been overlooked, owing to the difficulty in separating the constituents, recrystallisation from ordinary solvents either converting the carbanilino-*m*-nitrobenz*syn*aldoxime present into the *anti*-isomeride or else failing to effect a separation, or apparently failing to do so.

It was found that by means of chloroform (see experimental part) this difficulty could be overcome, and from the compound melting at 105°, diphenylcarbamide and carbanilino-*m*-nitrobenz*anti*aldoxime have been actually isolated without the necessity of warming the solution. In addition, washing with cold, very dilute

alkali removes a small quantity of *m*-nitrobenz*anti*aldoxime, which is also present in the mixture.

It has not been possible to isolate the carbanilino-*m*-nitrobenz*syn*aldoxime in a pure state from the mixture, but its presence is clearly indicated by the decomposition on keeping referred to above, an action quite characteristic of the carbanilino*syn*aldoximes.

The compounds melting at 75—78° and 148° yield, on hydrolysis with sodium hydroxide, in the former case, a small quantity of diphenylcarbamide, aniline, and *m*-nitrobenzonitrile and, in the latter, aniline and *m*-nitrobenz*anti*aldoxime. It therefore appears that the compound melting at 75—78° is pure carbanilino-*m*-nitrobenz*syn*aldoxime and the compound melting at 148° pure carbanilino-*m*-nitrobenz*anti*aldoxime, whilst the substance (m. p. 105°) described by Goldschmidt is a complex mixture containing *m*-nitrobenzaldoxime, the two carbanilino-derivatives, diphenylcarbamide, and possibly *m*-nitrobenzonitrile. The last two compounds are probably the decomposition products of carbanilino-*m*-nitrobenz*syn*aldoxime, produced at first in larger quantity, and decomposing during the twenty-four hours in which the reaction mixture was allowed to remain in the course of the preparation.

The production of a carbanilinobenz*syn*aldoxime from an *anti*aldoxime by means of phenylcarbimide is very extraordinary. Beckmann (*Ber.*, 1890, **23**, 3335) mentions that he obtained a small quantity of carbanilinobenz*syn*aldoxime from benz*anti*aldoxime and phenylcarbimide, a result which has been confirmed by the present authors (see below), but explains its formation by supposing that his benz*anti*aldoxime was impure and contained some benz*syn*aldoxime, a most unlikely contingency. There is no doubt that both Goldschmidt and Beckmann failed to realise the importance of this isolated experience of the latter or they would have recognised that the new compounds they were obtaining were probably mixtures.

An important confirmation of the views expressed above has been obtained by the study of the carbanilino-derivatives of *p*-dimethylaminobenzaldoxime (see Brady and Dunn, T., 1914, **105**, 2874) and of 3:4-dimethoxybenzaldoxime. Neither of these oximes can be obtained in the *syn*-form.

When *p*-dimethylaminobenz*anti*aldoxime is mixed in ethereal solution with phenylcarbimide, after a few seconds there is a copious precipitate of shining needles. If, after twenty-four hours, these are removed and recrystallised from cold acetone and water, a compound is obtained which is undoubtedly carbanilino-*p*-dimethylaminobenz*syn*aldoxime (m. p. 117°). On hydrolysis this

compound gives *p*-dimethylaminobenzonitrile and aniline as its chief decomposition products and a very small quantity of *p*-dimethylaminobenz*anti*aldoxime, formed probably through the transformation of a little of the *syn*-derivative into the *anti*-form during the heating. If this compound be boiled with alcohol under a reflux for an hour, on cooling, carbanilino-*p*-dimethylaminobenz*anti*aldoxime (m. p. 152°) separates.

This compound is also obtained if the solid carbanilino-*p*-dimethylaminobenz*syn*aldoxime is kept for some days, a little aniline, diphenylcarbamide, and *p*-dimethylaminobenzonitrile being formed simultaneously.

Carbanilino-*p*-dimethylaminobenz*anti*aldoxime, on heating with sodium hydroxide solution, is hydrolysed to *p*-dimethylaminobenz*anti*aldoxime and aniline, no nitrile being formed.

From 3:4-dimethoxybenz*anti*aldoxime the compound obtained by the action of phenylcarbimide is undoubtedly a mixture. In various experiments it melted in the neighbourhood of 94° or of 104°, a product of low melting point being always obtained when the precipitate was removed from the ethereal solution in which the reaction was carried out soon after it has been formed.

This compound behaves similarly to that obtained from *m*-nitrobenz*anti*aldoxime under the same conditions. Recrystallisation sometimes raises and sometimes lowers the melting point between the limits of 90° and 110°. The *syn*-derivative present does not decompose so readily as in other cases, and boiling with alcohol does not satisfactorily convert it into the *anti*-isomeride, neither does leaving it in contact with the mother liquor in the preparation for some days.

If the solid is kept for a week, however, it decomposes in the usual way, and from the product a compound is obtained which, after recrystallisation from alcohol several times, melts constantly at 129°. The same result is obtained by crystallising the crude product from alcohol and leaving the crystals in contact with the mother liquor for some days, one further crystallisation giving the compound melting at 129°.

The crude substance, on hydrolysis with alkalis, gives aniline, ammonia, 3:4-dimethoxybenzoic acid, and 3:4-dimethoxybenzaldoxime, there being about twice as much oxime as acid formed in the case of preparations melting at 104°, whilst in other cases where the crude product had a lower melting point the proportion of acid formed was greater.

The compound melting at 129°, on hydrolysis, gave aniline and 3:4-dimethoxybenzaldoxime, no nitrile, ammonia, or acid being detected.

In the case of the benzaldoximes themselves there is no doubt that benz*anti*aldoxime, on treatment with phenylcarbimide, yields at first a quantity of carbanilinobenz*syn*aldoxime [m. p. 77° (74° ?)] and afterwards a mixture of the two isomerides melting at 80—130°, according to the length of time the crystals are in contact with the mother liquor. The compound melting at 130°, after recrystallising from alcohol, melts constantly at 136°, and is identical with the compound considered by Goldschmidt to be carbanilinobenz*anti*aldioxime. It gives, on hydrolysis, aniline, benz*anti*aldoxime, and no nitrile. The substances of lower melting point all decompose on keeping, giving the usual products, namely, aniline, nitrile, and carbanilinobenz*anti*aldoxime.

By the action of phenylcarbimide on benz*syn*aldoxime in ether, Goldschmidt obtained a compound melting at 94° which he considered to be carbanilinobenz*syn*aldoxime. Beckmann, however, by keeping the solution cool (5°), obtained a substance melting at 74°, and by using benzene instead of ether as a solvent and warming gently, obtained the compound melting at 94° previously described by Goldschmidt. It would appear, therefore, that there were three carbanilinobenzaldoximes, one from the *anti*-oxime and two from the *syn*-oxime.

Goldschmidt failed to obtain the compound melting at 74°, but he recrystallised his product from ether and from warm benzene, and we have no information as to the purity of his reagents. Beckmann did not recrystallise his compound, and as it melted at 94° after washing with benzene on a porous tile, he was satisfied as to its purity. These experiments have been repeated by the present authors, and it has been found that it was unnecessary to cool the solution to obtain the pure carbanilinobenz*syn*aldoxime, provided that the starting materials were pure and dry and that the precipitate was filtered off at once.

From benz*syn*aldoxime and phenylcarbimide was obtained carbanilinobenz*syn*aldoxime (m. p. 77°) which gives on hydrolysis aniline and benzonitrile, and, on keeping, decomposes into aniline, diphenylcarbamide, benzonitrile, and carbanilinobenz*anti*aldoxime. Beckmann's experiment using warm benzene was also repeated, but the compound obtained proved to be, not the *syn*-, but the *anti*-derivative (m. p. 136°).

If carbanilinobenz*syn*aldoxime is recrystallised from warm solvents, products melting at 84° to 130° are obtained, according to the temperature employed and the length of time the solution is kept at that temperature.

The substances melting at lower temperatures, namely, 84° to 110°, all decompose when kept, on account of the *syn*-derivative still

present, giving the usual products. If the pure *syn*-derivative is boiled with alcohol for an hour, it is not converted into the isomeride, but is decomposed, aniline, diphenylcarbamide, and benzonitrile being the products of the reaction. If, however, the compound is recrystallised several times from benzene, the pure *anti*-isomeride is obtained. As a result of these investigations, the authors are of opinion that the compound described as melting at 94° is a mixture of the two isomerides, as in the case of the anomalous carbanilino-*m*-nitrobenzaldoximes.

There seems to be no doubt, therefore, that by the action of phenylcarbimide on the *anti*-oximes a certain quantity of carbanilino*syn*-derivative is produced, if, indeed, this compound is not the primary product of the reaction. The carbanilino*syn*aldoximes, on keeping, are decomposed, giving aniline, diphenylcarbamide, nitrile, and carbanilino*anti*-compound. Boiling with alcohol or leaving the crystals in contact with the mother liquor in the preparation also brings about isomeric change. On hydrolysis, the *syn*-derivatives resemble the acetyl derivatives of the *syn*-oximes, and give nitrile, aniline, and a small quantity of diphenylcarbamide.

$$\begin{aligned} \mathrm{R{\cdot}C{\cdot}H} \\ \mathrm{\overset{\|}{N}{\cdot}O{\cdot}CO{\cdot}NHPh} \end{aligned} = \mathrm{RCN + CO_2H{\cdot}NHPh}$$

$$\mathrm{CO_2H{\cdot}NHPh} = \mathrm{NH_2Ph + CO_2}$$

$$\mathrm{2CO_2H{\cdot}NHPh} = \mathrm{CO(NHPh)_2 + CO_2 + H_2O.}$$

The *anti*-derivatives give, as would be expected, the *anti*-oxime and aniline:

$$\begin{aligned} \mathrm{R{\cdot}C{\cdot}H} \\ \mathrm{NHPh{\cdot}CO{\cdot}O{\cdot}\overset{\|}{N}} \end{aligned} = \begin{aligned} \mathrm{R{\cdot}C{\cdot}H} \\ \mathrm{HO{\cdot}\overset{\|}{N}} \end{aligned} + \mathrm{NH_2Ph + CO_2.}$$

Goldschmidt claims as the result of his work that phenylcarbimide is a very valuable reagent for the determination of the configuration of the oximes; it will, however, be seen from the above considerations that it is quite useless for this purpose, as it may give identical compounds from both the *syn*- and *anti*-oximes.

Mention may be made of the fact that *o*-nitrobenz*anti*aldoxime behaves in an exactly similar manner to the *m*-nitro compound on treatment with phenylcarbimide, and that the compound described in the literature as carbanilino-*o*-nitrobenz*anti*aldoxime (m. p. 88°) is a mixture of the two isomerides, and that the pure compound melts at 117°. It is found that the carbanilino*anti*oximes melt at a higher temperature than the corresponding *syn*-derivatives, carbanilino-*o*-nitrobenz*anti*aldoxime being an apparent exception, but as carbanilino-*o*-nitrobenz*syn*aldoxime melts at 91°, this anomaly has now been removed.

An interesting analogy is provided by the action of ethyl chlorocarbonate on the sodium salts of the oximes. In the case of *p*-nitrobenz*anti*aldoxime the first product of the action is carbethoxy-*p*-nitrobenz*syn*aldoxime, $NO_2 \cdot C_6H_4 \cdot \overset{\displaystyle H}{\underset{\displaystyle N \cdot O \cdot CO_2Et}{\overset{\|}{C}}}$ (m. p. 94°), which gives, on hydrolysis, *p*-nitrobenzonitrile and subsequently *p*-nitrobenzoic acid, but no *p*-nitrobenz*anti*aldoxime. If this compound is boiled with alcohol or twice recrystallised from boiling alcohol, it is converted into carbethoxy-*p*-nitrobenz*anti*aldoxime (m. p. 109°), which, on hydrolysis, gives no nitrile or ammonia, but only *p*-nitrobenz*anti*aldoxime.

The action of ethyl chlorocarbonate on *m*-nitrobenz*anti*aldoxime and on *p*-dimethylaminobenz*anti*aldoxime has been investigated, but it has not been found possible so far to obtain the *syn*-derivative direct from the *anti*-oxime, the products on hydrolysis in each case giving the original oxime. The great readiness with which these compounds undergo isomeric change, a fact which has been noted in the case of the *p*-nitro-compound, probably accounts for the failure to isolate them.

Early in the investigations on the carbanilino-compounds, a number of diphenylcarbamyl- and carbanilino-derivatives of the hydroxybenzaldoximes were prepared. It was thought that a study of these compounds would help to solve the question of the carbanilino-*m*-nitrobenzaldoximes. Subsequent experience, however, suggested the course of investigation described above, and as nothing of particular interest was forthcoming, the study of these compounds was not further pursued.

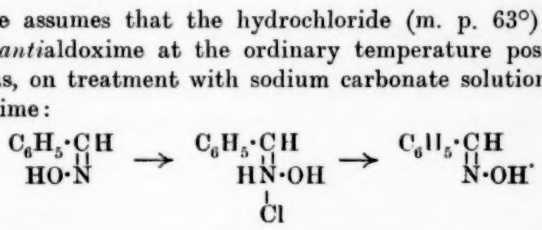
Before making any attempt to explain the formation of the carbanilino-derivatives, it is necessary to discuss the mechanism of change in the oximes themselves. There is but one general method by which the aromatic *anti*-aldoximes may be converted into their *syn*-isomerides, namely, through the intermediate formation of the hydrochlorides. In a considerable number of cases, however, this method fails, and it has not been found possible to prepare the *syn*-derivatives at all (see Brady and Dunn, T., 1914, **105**, 824). It may be mentioned that in a limited number of cases it is possible to convert the *anti*- into the *syn*-isomeride by the action of light (see Ciamician and Silber, *Ber.*, 1903, **36**, 4268; Brady and Dunn, T., 1913, **103**, 1620). This method, however, has only been tried in a few cases, and is being further investigated by the authors. Consequently the chief questions to be considered are the mechanism of the isomerisation via the hydrochloride, and the reverse change by which the *syn*- pass over to the *anti*-derivatives, a reaction which

takes place slowly even in the solid state (compare Brady and Dunn, *loc. cit.*), and more rapidly in solution or in the presence of traces of mineral acids.

On the analogy of the *cis-trans*-isomerides of the ethylene series the most probable explanation of the change from one form of the oxime to the other involves the rupture of the carbon–nitrogen double bond; indeed, it seems inexplicable to the authors that the change could take place without this occurring.

Now it has been generally assumed, in agreement with Luxmore (T., 1896, **69**, 183), that in the case of the formation of the hydrochloride of, for example, benzaldoxime, the addition of hydrogen chloride takes place at the nitrogen atom which becomes quinquevalent.

Luxmore assumes that the hydrochloride (m. p. 63°) obtained from benz*anti*aldoxime at the ordinary temperature possesses the *syn*-form as, on treatment with sodium carbonate solution, it gives the *syn*-oxime:



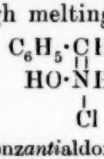
He has, moreover, shown that, by cooling the ethereal solution of benz*anti*aldoxime to 0° before passing in hydrogen chloride, a second hydrochloride (m. p. 105°) can be obtained, which he regards as the *anti*-compound on account of its regenerating the *anti*-oxime with sodium carbonate solution:

This compound, on recrystallising from chloroform, changes readily into the hydrochloride melting at 63°.

If Luxmore's views are accepted, there is no explanation of the formation of the *syn*-oxime through the hydrochloride of lower melting point if the breaking of the double bond is considered a condition of the isomeric change.

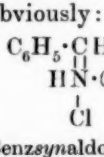
This work has been repeated by the present authors, and the existence of the compound described by Luxmore confirmed. This hydrochloride (m. p. 105°), on decomposition with sodium carbonate solution, gives mainly benz*anti*aldoxime, although a little benz*syn*-aldoxime is also produced, due probably to change to the stable hydrochloride of lower melting point during the decomposition. In addition, however, a third hydrochloride (m. p. 103°) has been obtained by acting on benz*syn*aldoxime at a low temperature. This compound is obviously different from the hydrochloride melting

at 63°, and the action of sodium carbonate distinguishes it from the hydrochloride obtained by Luxmore from benz*anti*aldoxime. The latter, on decomposition with this reagent, invariably gives an oil consisting largely of benz*anti*aldoxime and very little benz*syn*aldoxime, whilst the former always gives a solid consisting of benz*syn*aldoxime and very little benz*anti*aldoxime. The two hydrochlorides of high melting points are obviously:



Benz*anti*aldoxime hydrochloride.

and

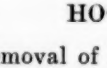


Benz*syn*aldoxime hydrochloride.

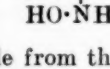
and the third hydrochloride (m. p. 63°) a compound in which the carbon–nitrogen double bond is broken.

Evidence has also been obtained of a similar phenomenon in the case of the *p*-nitrobenzaldoxime hydrochlorides.

If benz*anti*aldoxime is regarded as having the constitution the addition of hydrogen chloride at the double bond can take place in two ways:



and



In the removal of hydrogen chloride from the first of these compounds a change in the relative position of the hydrogen atom and the hydroxyl group would take place only if a hydrogen atom were removed different from that originally combined with the chlorine, whilst, in the second formula, the removal of hydrogen chloride would not affect the relative position of the groups.

The action of methyl iodide on the sodium salt of benz*syn*aldoxime has already been discussed (compare Brady, T., 1914, **105**, 2104),* and it would seem that in this case the addition of methyl iodide takes place in such a way that the methyl group remains attached to the nitrogen atom. If, therefore, the reactions are analogous, the second formula above is the more probable for the hydrochloride. On the other hand, if this is the case, there is no satisfactory explanation of the transformation of the *anti*-

* In this paper, one of us was at variance with the work of Hartley and Dobbie as regards the existence of a band in the absorption spectrum of benzaldoxime. The presence of the band found by these investigators has since been confirmed by Dobbie and Fox (private communication), and by Purvis (T., 1914, **105**, 2496). There seems, therefore, to be no reason to doubt its existence. This mistake does not in any way vitiate the conclusions drawn from the observations, as only the shift of the absorption towards the visible end of the spectrum was under consideration.

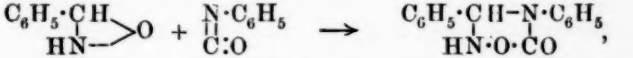
into the *syn*-isomeride through the hydrochloride. In addition, some explanation is required for the production of some carbanilino-*syn*-oxime by the action of phenylcarbimide on the *anti*-oxime, of the action of ethyl chlorocarbonate on the sodium salt of the *anti*-isomeride giving the carbethoxy-*syn*-derivative, and of the action of diphenylcarbamyl chloride on the sodium salt of both oximes giving the diphenylcarbamyl-*syn*-oxime (see Brady and Dunn, T., 1913, **103**, 1614).

All these reactions and many others of the oximes can be co-ordinated and brought into line with the action of methyl iodide if it is considered that the oximes and their sodium salts are tautomeric substances and capable of reacting in the forms:

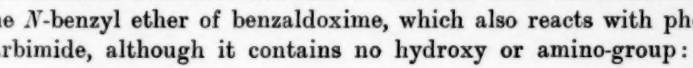
Benz*anti*aldoxime. Benz*syn*aldoxime.

The question of the carbanilino-derivatives will be considered first.

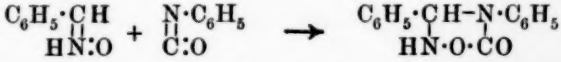
Beckmann (*loc. cit.*), adopting his *iso*oxime structure, considers that in the case of benz*syn*aldoxime the addition of phenylcarbimide takes place in the following manner:



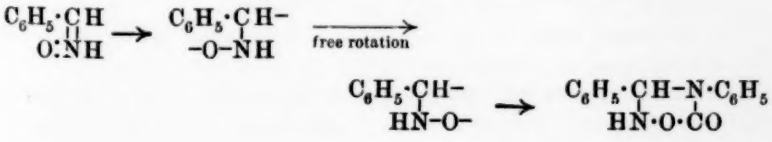
and adduces evidence that this is the case from the behaviour of the *N*-benzyl ether of benzaldoxime, which also reacts with phenylcarbimide, although it contains no hydroxy or amino-group:



If, instead of Beckmann's *iso*oxime structure the tautomeric structure $C_6H_5\cdot C(H)\!=\!N(H)\cdot O$, is employed, the final product will have the same structure, the carbon–nitrogen and the nitrogen–oxygen double bonds both breaking and the oximino–nitrogen becoming tervalent:



In the case of benz*anti*aldoxime, the action will be as follows:



that is, the product will be the same as that obtained from benz-*syn*aldoxime. If rotation does not take place in the second stage the product will be an optical isomeride of the first compound, as the oximino-carbon atom is asymmetric. Indeed, the formation of the carbanilino-derivative from the *syn*-oxime would probably lead to a mixture of two optical isomerides. Unfortunately, there seem to be insuperable difficulties in the study of this question, as the carbanilino*syn*aldoximes are so unstable, and, being neutral substances, salts with active acids and bases cannot be obtained. The introduction of basic or acidic groups into the benzene nucleus is precluded by the influence these have on the stability of the *syn*-oximes (see below).

It is noteworthy that on mixing an ethereal solution of benz-*syn*aldoxime with phenylcarbimide there is an immediate precipitation of the carbanilino-derivative and very little of the substance remains in solution, that is, the *syn*-oxime presents the most favourable structure for the formation of a carbanilino-derivative as it does for the formation of a *N*-ether (see Brady, *loc. cit.*). On the other hand, an ethereal solution of benz*anti*aldoxime gives, after a few seconds, a small quantity of precipitate of a carbanilino-derivative identical with that obtained from benz*syn*aldoxime.

The amount of carbanilinobenz*syn*aldoxime obtained from the *anti*-oxime increases according to the length of time the reaction mixture is left (a fact not observed by Beckmann), although after a time the precipitate is contaminated with carbanilinobenz*anti*-aldoxime, due probably to change of the cyclic compound. These phenomena are observed in the case of other *anti*- and *syn*-oximes.

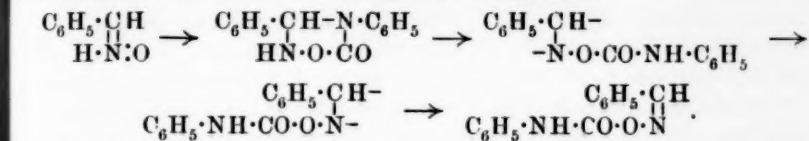
An explanation can easily be provided. It seems that the *anti*-oximes exist mainly in the form R·CH:N·OH (compare the action of methyl iodide) and the phenylcarbimide reacts only with the small amount of the tautomeric form present and the sparingly soluble carbanilino-derivative is precipitated. This disturbs the equilibrium, and more of the compound R·CH:NH:O is formed, which is in turn acted on by phenylcarbimide. Carbanilinobenz-*syn*aldoxime changes very readily into carbanilinobenz*anti*-aldoxime:

$$\begin{array}{l} C_6H_5\cdot CH\!-\!\overset{+}{N}\cdot C_6H_5 \\ \quad\times\quad | \quad\quad | \\ \quad HN\cdot O\cdot CO \end{array} \longrightarrow \begin{array}{l} \quad\quad\quad C_6H_5\cdot CH \\ \quad\quad\quad\quad\quad || \\ C_6H_5\cdot NH\cdot CO\cdot O\cdot N \end{array}.$$

The hydrogen atom (×) wanders to the nitrogen atom (+) and the double bond in the oximino-group is obtained.

If this reaction is followed by means of models, it will be found that the new bond between carbon and nitrogen will be different

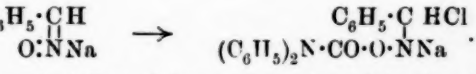
from that originally broken, and the reaction will result in the reversal of the relative positions of the groups:



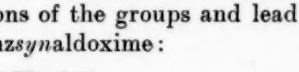
It is of interest that when this change takes place in the solid state it is always accompanied by decomposition of part of the compound with the formation of diphenylcarbamide, aniline, and nitrile. This would not be expected if the reaction merely consisted of isomeric change.

With reference to the fact that the *syn*-oximes probably exist mainly in the tautomeric form, R·C(:NH):O, may be mentioned the action of diazomethane. This reagent reacts readily with *anti*-oximes to give the corresponding *o*-methyl ether, but is without action on the *syn*-oximes (Forster and Dunn, T., 1909, **95**, 425).

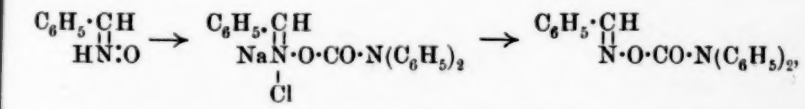
The action of diphenylcarbamyl chloride on the sodium salts of the oximes will resemble that of methyl iodide, except that both the carbon–nitrogen and the oxygen–nitrogen double bonds are broken:



If this reaction is followed by means of models, it will be seen that the loss of sodium chloride from the above compound will alter the relative positions of the groups and lead to the formation of diphenylcarbamylbenz*syn*aldoxime:



conversely, the sodium salt of the *syn*-oxime would yield diphenylcarbamylbenz*anti*aldoxime. This has been found not to be the case, as the same diphenylcarbamyl derivative is obtained from both sodium salts. It is, however, possible that steric hindrance prevents the large diphenylcarbamyl group taking up its position next to the phenyl group, and that in this case only the nitrogen–oxygen double bond is broken with the formation of the stable *syn*-derivative:



(compare the action of methyl iodide on the sodium salt of benz-*anti*aldoxime, *loc. cit.*).

It is, however, not possible to decide if diphenylcarbamyl chloride reacts with the sodium salt of the *syn*-oxime. The reaction must be carried out in the cold to avoid isomeric change as much as possible, and this necessitates a prolonged treatment. During this time a certain amount of the sodium salt will undergo change into the *anti*-isomeride, which will react with the diphenylcarbamyl chloride, and the diphenylcarbamyl derivative produced in the reaction may be entirely from this source.

Hantzsch has found that the action of acetyl chloride on an ethereal solution of the *anti*-oximes yields a mixture of the acetyl derivative of the *anti*-oxime and of nitrile. He presumed that the hydrogen chloride formed during the reaction converted some of the *anti*-oxime into the *syn*-oxime, and that the latter was acetylated and subsequently lost acetic acid, giving the nitrile. This explanation does not seem satisfactory in the case of those oximes which are not converted into *syn*-derivatives by means of hydrogen chloride. If, however, the reaction is additive:

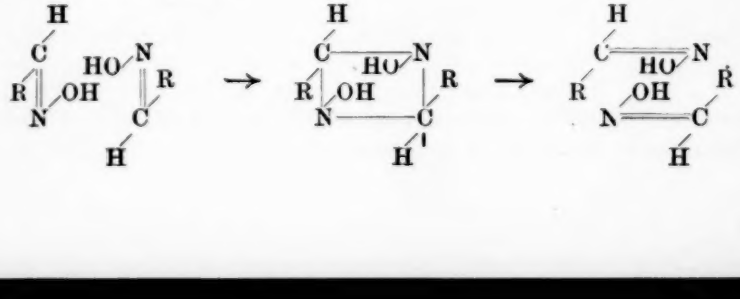
$$C_6H_5\cdot CH \underset{O:NH}{\overset{\|}{}} \longrightarrow C_6H_5\cdot CHCl \underset{AcO\cdot NH}{\overset{|}{}} \longrightarrow C_6H_5\cdot CH \underset{N\cdot OAc'}{\overset{\|}{}}$$

the removal of hydrogen chloride will give the acetyl derivative of the *syn*-oxime and hence the nitrile. The hydrogen chloride formed during the reaction will, however, convert some of the unstable acetyl-*syn*-oxime into its isomeride.

In the case of the acetylation by means of the compound of acetyl chloride and pyridine (see Brady and Dunn, T., 1915, **107**, 1861), in which the pure acetyl-*anti*-oxime is obtained, the reaction is unlikely to be an additive one, and the *anti*-oxime reacts in the enolic form. Acetic anhydride, which also gives the pure acetyl derivative, is added, probably only at the oxygen–nitrogen double bond:

$$C_6H_5\cdot CH \underset{O:NH}{\overset{\|}{}} + Ac_2O \longrightarrow C_6H_5\cdot CH \underset{(AcO)_2NH}{\overset{\|}{}} \longrightarrow C_6H_5\cdot CH \underset{Ac_2O\cdot N}{\overset{\|}{}}.$$

The spontaneous change of the *syn*-oximes and of their acetyl, methyl, and other derivatives into the *anti*-isomerides is to be explained on the supposition that the isomeric change of the labile into the stable forms in the case of the oximes is due to association into double molecules:



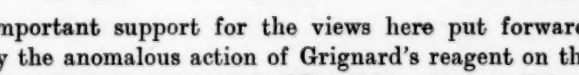
This is the theory advanced by Stewart to account for the conversion of ethenoid and azethenoid isomerides (P., 1905, **21**, 73). The marked catalytic action of traces of hydrogen chloride on the conversion of the *syn*- into the *anti*-isomeride and the action of solvents in increasing the speed of the change may be due to the effect of residual affinity disturbing the double bond of the oximino-group and leading to the more ready formation of the double molecule.

The action of sunlight in converting some *anti*-oximes into the unstable *syn*-isomerides admits of a similar explanation. It is interesting to note in this connexion that a very general effect of sunlight in organic compounds is to induce polymerisation (Ciamician and Silber, *Ber.*, 1902, **35**, 4128; 1903, **36**, 1575; and others). Moreover, Beckmann (*Ber.*, 1888, **21**, 766), in determining the molecular weights of certain oximes in benzene solution by the cryoscopic method, found that acetoxime and camphoroxime gave double, and benzaldoxime and anisaldoxime one and a half times, the normal values. In acetic acid solution, however, normal results were obtained, as was also the case when the molecular weights were determined by the lowering of the vapour tension of an ethereal solution (*Ber.*, 1888, **21**, 1163).

The change from the *anti*- into the *syn*-isomeride through the hydrochloride can now be explained. The addition here takes place at both double bonds:

A different hydrogen atom from that originally combined with chlorine is now removed with sodium carbonate, and consequently the relative positions of the groups are altered with the formation of the *syn*-oxime.

The action of cuprous chloride on benz*anti*aldoxime, giving an additive product which with alkalis gives benz*syn*aldoxime (Comstock, *Amer. Chem. J.*, 1897, **19**, 485), can also be explained on this assumption.



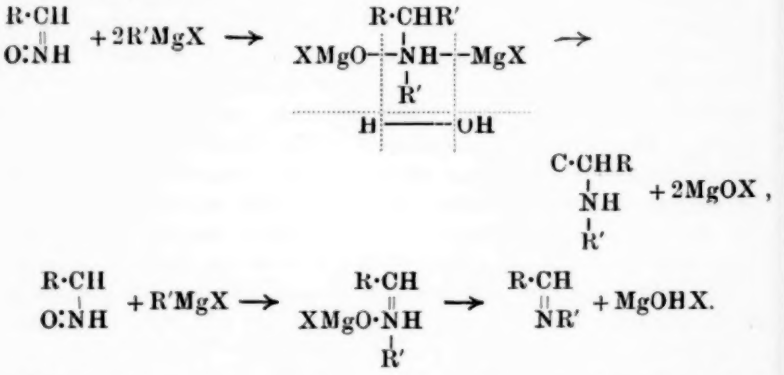
An important support for the views here put forward is provided by the anomalous action of Grignard's reagent on the oximes (Busch and Hobein, *Ber.*, 1907, **40**, 2096). As is well known, this reagent is decomposed by compounds containing a hydroxyl group with the formation of the corresponding hydrocarbon. This is not, however, the case with the oximes; benz*anti*aldoxime, for example, giving, with magnesiumphenylbromide, diphenylanilinomethane;

and, with magnesium-α-naphthylbromide, benzylidene-α-naphthylamine:

$$C_6H_5\cdot CH{:}N\cdot OH + 2C_6H_5\cdot MgBr + H_2O \longrightarrow (C_6H_5)_2CH\cdot NH\cdot C_6H_5 + 2MgOHBr$$

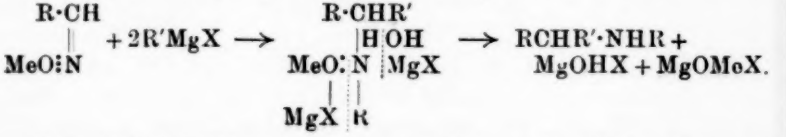
$$C_6H_5\cdot CH{:}N\cdot OH + C_{10}H_7MgBr \longrightarrow C_6H_5\cdot CH{:}N\cdot C_{10}H_7 + MgOHBr.$$

It seems to the authors that these reactions are best explicable on the lines indicated above, the oxime reacting in the tautomeric form, $C_6H_5\cdot CH{:}NH{:}O$.



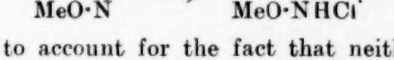
The failure of a second molecule of magnesium-α-naphthylbromide to react may be ascribed to steric influences, the first naphthyl group preventing the approach of a second to the double bond.

The action of Grignard's reagent on the *O*-methyl ethers of the oximes resembles the action of this reagent on esters, benz*anti*-aldoxime methyl ether and magnesium phenyl bromide giving diphenylanilinomethane. This reaction in itself is unusual, as the alkyl derivatives of such a substance as phenol, which is of a more acidic nature than benzaldoxime, are not acted on by magnesium-phenyl bromide. An explanation is possible if it is admitted that the two supplementary valencies of the oxygen and nitrogen atoms satisfy one another, that is, that the oxygen is quadrivalent and the nitrogen still quinquevalent in the *O*-ethers of the oximes:



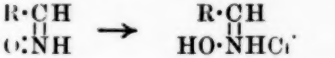
There is undoubtedly evidence for the quadrivalent nature of the oxygen atom in ethers in the compounds which they form with magnesium alkyl haloids. In addition, it is of interest to notice that it is impossible to obtain hydrochlorides of the *O*-methyl

ethers of the benzaldoximes by the usual means, whereas the normal structure would call for the existence of such compounds:

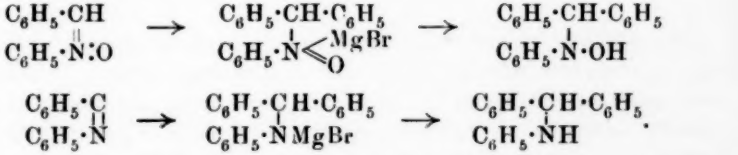


It is difficult to account for the fact that neither the oxygen–nitrogen triple bond nor the carbon–nitrogen double bond is ruptured by the action of hydrogen chloride, but it must not be forgotten that in the formation of hydrochlorides from the oximes themselves on the lines proposed by the present authors a hydroxyl group is produced which is not possible in the case of the ethers:

The question of the formation of a hydrochloride of the ammonium type from the oximes is discussed below.

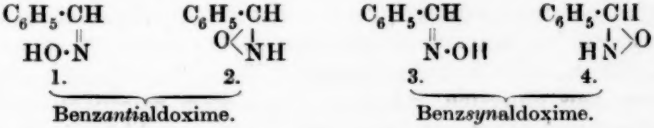


It is important to compare these reactions with the action of magnesium phenyl bromide on *N*-phenylbenzaldoxime and on benzylideneaniline (compare Angeli, Alessandri, and Aiazzi-Mancini, *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 546). In the former case, β-phenyl-β-diphenylmethylhydroxylamine is produced, and in the latter, diphenylanilinomethane:



It must be admitted, however, that in the first case it is to be expected that a second molecule of magnesiumphenyl bromide would react with the N:O group.

Beckmann (*loc. cit.*) has considered the possibility of tautomerism among the oximes, and the structures he has suggested will explain in a similar manner many of the reactions here treated:



Here the difference between compounds 2 and 4 is not in the relative positions of the oxygen and hydrogen atoms, but between the two hydrogen atoms.

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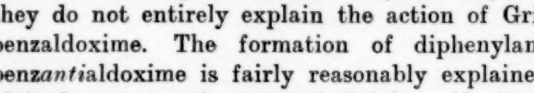
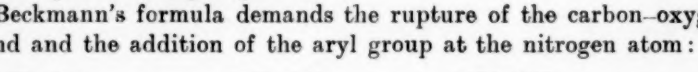
These formulæ, however, do not show why only one *N*-ether is obtainable, neither do they explain the failure to resolve that ether into two optical isomerides (see Brady, *loc. cit.*). Moreover, they do not entirely explain the action of Grignard's reagent on benzaldoxime. The formation of diphenylanilinomethane from benz*anti*aldoxime is fairly reasonably explained, but it is not so plain how magnesium α-naphthyl bromide leads to the formation of benzylidene-α-naphthylamine.

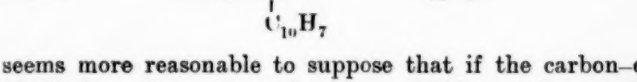
Beckmann's formula demands the rupture of the carbon–oxygen bond and the addition of the aryl group at the nitrogen atom:



It seems more reasonable to suppose that if the carbon–oxygen bond is broken the new aryl group would remain attached to carbon:



on the analogy of the action of magnesium methyl iodide on benzonitrile oxide:



The possible quinquevalency of the nitrogen atom in the oximes is of great interest in view of other investigations on the stereochemistry of nitrogen. It has been shown, in a number of tervalent nitrogen compounds which have been studied with the object of resolution into optically active isomerides, that the three valency directions of the nitrogen atom in such compounds as, for example, ammonia, probably lie in one plane. Now a fundamental condition of the Hantzsch-Werner hypothesis is that the valency direction attached to the hydroxyl group lies outside the plane of the double bonds. Evidence that this is the case has been supplied by the work of Mills and Bain (T., 1910, **97**, 1866).

It is therefore questionable whether the nitrogen atom in the oximes can be regarded as tervalent in the sense of the nitrogen atom in ammonia and the amines. The quinquevalent structure removes this objection, but it does not seem reasonable to assign a quinquevalent structure to the *O*-ethers, which also exist in isomeric forms.

One further point remains to be considered, namely, the failure to obtain the *syn*-isomerides of a considerable number of sub-

stituted benzaldoximes. The following table gives the benzaldoximes which have been specially investigated:

Benzaldoximes where two isomerides have been obtained.	*Benzaldoximes where it has not, so far, been possible to obtain a syn-isomeride.*
Benzaldoxime.	*o*-, *m*-, and *p*-Hydroxybenzaldoximes.
o-, *m*-, and *p*-Nitrobenzaldoximes.	Vanillinoxime.
o-, *m*-, and *p*-Chlorobenzaldoximes.	5-Bromovanillinoxime.
m- and *p*-Bromobenzaldoximes.	5-Nitrovanillinoxime.
p-Iodobenzaldoxime.	*o*-Methoxybenzaldoxime.
3 : 4-Dichlorobenzaldoxime.	Veratraldoxime.
p-Cyanobenzaldoxime.	*o*-Aminobenzaldoxime.
m- and *p*-Methylbenzaldoximes.	*p*-Dimethylaminobenzaldoxime.
Cuminaldoxime.	
Mesitylaldoxime.	
m- and *p*-Methoxybenzaldoximes.	
p-Ethoxybenzaldoxime.	
Piperonaldoxime.	
p-Acetoxybenzaldoxime.	
Dihydrobenzaldoxime.	

The second group contains only those oximes which have been actually studied by the present authors.

It will be seen from the above table that it is difficult to lay down any definite conditions regulating the existence of a second isomeride. Substitution in the ortho-position seems to hinder isomeric change, and meta-substitution has the same effect in a smaller degree. *o*-Methoxybenzaldoxime exists in the *anti*-form only, *m*-methoxybenzaldoxime gives a very unstable *syn*-derivative which, unlike *p*-methoxybenz*syn*aldoxime, cannot be obtained in the pure state.

On the other hand, all three nitro- and chloro-benzaldoximes exist in two forms. The introduction of a hydroxyl group into the benzene nucleus inhibits the formation of a *syn*-isomeride, even if a favourable group (for example, NO_2) is also present (Brady and Dunn, T., 1915, **107**, 1858). Moreover, so little difference as the acetylation of the phenolic hydroxyl group in *p*-hydroxybenzaldoxime makes it possible to obtain two isomerides from this compound (Brady and Dunn, T., 1914, **105**, 823).

This rather points to the acidic nature of the substituting group having an important influence, especially in view of the catalytic action of the hydrogen ion in transforming the *syn*- into the *anti*-isomeride, but a neutral group such as methoxyl in certain positions has the same inhibitive effect, whilst the acidic nitro-group does not so behave to such a marked degree. The mere difference of attraction of the variously substituted benzene nuclei for the hydroxyl in the oximino-group does not seem a sufficient explanation in itself, as it is difficult to imagine that there would be such a marked difference between the para- and the ortho- or meta-methoxy-substituted ring; again, so notable a distinction would

scarcely be expected between *p*-hydroxy- and *p*-acetoxy-benzaldoxime. Steric hindrance cannot well be cited as an important influence if interpreted in the usual sense, as an ortho-substituent in the benzene ring would then tend to render the *syn*-isomeride more stable, whereas the opposite is the case.

From the authors' experiments on the acetylation of the hydroxybenzaldoximes it is evident that the position of the substituting group affects the basicity of the oximino-group; *o*- and *m*-hydroxyaldoximes yield only monoacetyl derivatives in which the oximino-group is acetylated, but *p*-hydroxybenzaldoxime yields a diacetyl derivative and in addition gives a monoacetyl derivative in which the phenolic and not the oximino-group is acted on. The introduction of a methoxyl group into *p*-hydroxybenzaldoxime in the meta-position with respect to the oximino-group (giving vanillinoxime) has the effect of rendering the oximino-group more readily attacked, and, whilst a diacetyl derivative can still be obtained, the monoacetyl compound has the oximino-group acetylated (Brady and Dunn, T., 1914, **105**, 2411).

Now it has been shown above that the addition of hydrogen chloride to the *anti*-oxime can take place in two ways:

$$\begin{array}{l} X\cdot C\cdot H \\ \quad\| \\ O:N\cdot H \end{array} \longrightarrow \begin{array}{l} X\cdot C(Cl)\cdot H \\ \quad| \\ HO\cdot N\cdot H \end{array} \quad \text{or} \quad \begin{array}{l} X\cdot C\cdot H \\ \quad\| \\ HO\cdot N\cdot HCl \end{array}$$

The first of these hydrochlorides, on decomposition with sodium carbonate solution, yields the isomeric oxime, whilst the second regenerates the original *anti*-oxime. It seems, therefore, probable that those hydrochlorides which do not yield a *syn*-oxime on decomposition with sodium carbonate exist only in the second, or ammonium, form. Now the influence of the position of substituting groups which renders the oximino-group more readily attacked by acetic anhydride will probably facilitate the formation of the ammonium type of hydrochloride rather than that in which the carbon–nitrogen double bond is ruptured, and consequently the isomeride will not be formed through the hydrochloride in the usual way.

The influence of the residual affinity of such radicles as the nitro-group must not be overlooked. The effect of such residual affinity on the unsaturated carbon–nitrogen complex may lead to a weakening of the double bond and consequent greater facility for the addition of hydrogen chloride at this point giving the *syn*-forming hydrochloride.

The effect, therefore, of substituting groups in the benzaldoximes on the relative stability of the two isomerides is probably an additive function, steric hindrance, attraction of the substituting group for the hydroxyl group, the residual affinity of the sub-

stituting group, and the effect of the group and its position on the basicity of the oximino-complex all determining the existence or non-existence of the *syn*-isomeride. It must be remembered that these are only predisposing causes and that the actual result is probably due to an accumulation or balance of these causes, some of them by themselves may exert but a trifling effect, but when combined have sufficient force to determine the non-existence of the *syn*-isomeride. It is of interest to note that steric hindrance and increased acidity of the molecule undoubtedly has some effect on the formation of hydrochlorides, as is evidenced by 6-nitropiperonaloxime. This compound is diortho-substituted with respect to the oximino-group, the nitropiperonyl residue is strongly acidic, and the oxime is unique in giving no hydrochloride (Brady and Dunn, T., 1915, **107**, 1859).

It must be confessed that the question is by no means definitely decided, especially as the fact that there appear to be so many influences at work makes it difficult, if not impossible, to decide whether any particular substituted benzaldoxime can be obtained in two isomeric forms. As a result of these investigations, however, it seems likely that it will be along some such lines as have been indicated that the final solution of the problem will be attained.

In conclusion, the authors wish to point out that they are aware that the ideas here put forward can only be tentatively accepted, as they open up vistas of a very large amount of experimental work before a definite pronouncement can be made. As this investigation has of necessity been interrupted for the time being, the authors consider that the results they have obtained in their work on this subject during the last few years are sufficiently suggestive to claim consideration for the theories here outlined.

Experimental.

Action of Phenylcarbimide on the m-*Nitrobenzaldoximes.*

m-Nitrobenz*anti*aldoxime was dissolved in dry ether in a stoppered bottle, an equivalent molecular quantity of phenylcarbimide added, and the mixture allowed to remain for twenty-four hours. At the end of that time the majority of the carbanilino-derivative had crystallised out in masses of stellated needles. The solid was separated and found, in various experiments, to melt and decompose in the neighbourhood of 105°. This substance was boiled with alcohol for one hour under reflux, the reaction mixture diluted slightly with water, and allowed to cool, when carbanilino-*m*-nitrobenz*anti*aldoxime separated; after recrystallisation twice from alcohol it was obtained in short, straw-coloured prisms melting and

decomposing at 148° (Goldschmidt, *loc. cit.*, gives 139°). Carbanilino-*m*-nitrobenz*anti*aldoxime was heated for three hours with 2*N*-sodium hydroxide solution. A small quantity of substance did not dissolve, and this could be separated by crystallisation from alcohol into unaltered carbanilino-compound and diphenylcarbamide. The alkaline solution had a strong odour of aniline and responded to the usual tests for that compound. On acidifying, a precipitate was obtained which was shown to be almost pure *m*-nitrobenz*anti*aldoxime.

The compound melting at 105° was washed with a little cold, very dilute sodium hydroxide solution, the alkaline solution acidified and extracted with ether, and the solid obtained after removing the ether was proved to be *m*-nitrobenz*anti*aldoxime. Recrystallisation of the residue from alcohol or acetone failed to separate the constituents; indeed, it is difficult to remove diphenylcarbamide when present as an impurity by recrystallisation from these solvents.

Treatment with a minimum of cold chloroform, however, left a residue which, after recrystallisation from alcohol, was found to be diphenylcarbamide. The chloroform solution, after evaporation in a current of air, yielded a solid which, after one recrystallisation from cold acetone and water, consisted of pure carbanilino-*m*-nitrobenz*anti*aldoxime. The mother liquors from this crystallisation, on further dilution, deposited a solid of low melting point; it was not, however, found possible to isolate any pure compound from this.

On leaving the compound melting at 105° for some days, either in a closed bottle or in the open air, or in an exhausted desiccator, decomposition took place, and the substance had a strong odour of aniline. The product was washed with dilute hydrochloric acid and the aniline identified in the filtrate by the usual methods. The solid was treated with warm chloroform and the solution filtered. The sparingly soluble residue was almost pure diphenylcarbamide, and after recrytallisation from alcohol melted at 232°. The solution was evaporated to dryness and the solid so obtained sintered at 102° and melted at 104°. This compound was recrystallised from alcohol and divided into three fractions:

1.	2.	3.
M. p. 136° gave aniline and *m*-nitrobenz*anti*aldoxime with potassium hydroxide. When crystallised from alcohol, it melted at 148°, and was carbanilino-*m*-nitrobenz*anti*aldoxime.	Sintered at 104°, melted at 110°. When crystallised twice from alcohol it melted at 115°, and when mixed with *m*-nitrobenzonitrile, at 116°. When boiled with sodium hydroxide it gave ammonia and *m*-nitrobenzoic acid.	Sintered at 105°, and had no definite melting point.

This decomposition on keeping is characteristic of the carbanilino*syn*aldoximes.

In a subsequent experiment on the action of phenylcarbimide on *m*-nitrobenz*anti*aldoxime, the crystalline compound that separated was left for three weeks in contact with the mother liquor. At the end of that time the crystals had become opaque, and, after pressing on a porous tile, melted at 147° and consisted of nearly pure carbanilino-*m*-nitrobenz*anti*aldoxime. This confirms the result of Goldschmidt. If to an ethereal solution of *m*-nitrobenz*syn*aldoxime an equivalent quantity of phenylcarbimide is added, after a few minutes a copious precipitation of carbanilino-*m*-nitrobenz*syn*aldoxime (m. p. 94°) takes place as described by Goldschmidt. This compound, on keeping, slowly decomposed with the formation of aniline, diphenylcarbamide, *m*-nitrobenzonitrile, and carbanilino-*m*-nitrobenz*anti*aldoxime, these being isolated and identified by the method described above.

*Action of Phenylcarbimide on o-nitrobenz*antialdoxime.

o-Nitrobenz*anti*aldoxime was dissolved in dry ether and one molecular proportion of phenylcarbimide was added. The carbanilino-compound did not separate out, so after twenty-four hours the ether was removed by a current of dry air. The product so obtained was of a semi-solid nature, and was therefore pressed on a porous plate and left for some days. At the end of that time it had set to a hard solid and there was a distinct odour of aniline. From this, by recrystallisation from alcohol, were isolated diphenylcarbamide and carbanilino-*o*-nitrobenz*anti*aldoxime melting at 117°. (Found N = 15·1; Calc. N = 14·8 per cent.). The melting point of this compound has been previously stated to be 88°, but the substance so described was probably the mixture of *anti*- and *syn*-isomerides. Carbanilino-*o*-nitrobenz*anti*aldoxime was hydrolysed by boiling for three hours with 2*N*-sodium hydroxide. On acidifying the solution, *o*-nitrobenz*anti*aldoxime was obtained, whilst aniline could be isolated from the mother liquor.

*Action of Phenylcarbimide on Benz*antialdoxime.

Equivalent quantities of benz*anti*aldoxime and phenylcarbimide were mixed in ethereal solution. After a few minutes a small quantity of crystalline substance separated which melted at 74° and proved to be carbanilinobenz*syn*aldoxime, being hydrolysed by alkalis to aniline and benzonitrile. The filtered solution at the end of an hour yielded another crop of crystals which sintered at 78°, and melted completely at 96°. The final crop, after six hours, was rather viscid, so it was washed with ether on a porous

tile, when it was found to melt at 104°. This compound was obviously a mixture. It was recrystallised from cold acetone and water, the major fraction still melted at 104°, but a very small second fraction melted fairly sharply at 78° and was carbanilinobenz*syn*aldoxime. The fact that recrystallisation did not raise the melting point was not unusual, since, as has been pointed out above, these mixtures are very difficult to purify by recrystallisation. The major fraction, when treated with cold chloroform, gave a residue which melted at 224° and was mainly diphenylcarbamide. The chloroform solution was evaporated to dryness and the solid was found to melt at 95°. This was treated with a small quantity of cold alcohol; the undissolved portion then melted at 128°, it gave no ammonia or odour of benzonitrile on boiling with alkalis, and consisted of carbanilinobenz*anti*aldoxime. In a second experiment, the benz*anti*aldoxime and phenylcarbimide were left together in ethereal solution for seven days. At the end of that time the crystalline product was collected and pressed on a porous tile. The crude substance melted at 132° and after one crystallisation at 136°; this was carbanilinobenz*anti*aldoxime.

Carbanilinobenz*syn*- and carbanilinobenz*anti*-aldoxime, as described, were hydrolysed with alcoholic sodium hydroxide on the water-bath for ten minutes. In the case of the compound melting at 74°, the alkaline solution was acidified and extracted with ether. The ethereal solution on evaporation gave an oil with the characteristic odour of benzonitrile, and on boiling with concentrated alkali was hydrolysed to ammonia and benzoic acid. From the acid solution aniline was isolated and identified in the usual way. In the case of the compound melting at 136°, the alkaline solution was diluted and extracted with ether, the ethereal solution shaken with dilute hydrochloric acid to remove aniline, and evaporated. A very small amount of a brown oil was obtained which lacked the odour of benzonitrile and gave no ammonia with alkalis. The aqueous solution was acidified and extracted with ether, when, after drying the extract and evaporating, an oil was obtained which, after a day, set to a mass of the characteristic crystals of benz*anti*aldoxime (m. p. 36°). These results confirm those of Beckmann, but it was found, in contradiction to Beckmann's statement, that carbanilinobenz*syn*aldoxime could be recrystallised from ether or warm benzene without decomposition. If, however, this compound is boiled with benzene when recrystallising, the recovered product is obviously not homogeneous under the microscope, and now melts at 84°. The second crop of crystals from such a solution sinters at 78° and melts completely only at 100°.

*Action of Phenylcarbimide on Benz*syn*aldoxime.*

Pure benz*syn*aldoxime (m. p. 132°) was dissolved in dry ether and an equimolecular proportion of phenylcarbimide added. There was an immediate precipitate of carbanilinobenz*syn*aldoxime, which was collected and pressed on a porous tile. This compound melted sharply and decomposed at 77°. The lower melting point obtained by Beckmann, namely, 74°, was probably due to the employment of a less pure benz*syn*aldoxime. It is unnecessary to cool the ethereal solution to 5° as stated by Beckmann. Carbanilinobenz*syn*aldoxime was boiled with alcohol for an hour under reflux and, on cooling, diphenylcarbamide separated out. The solution was diluted with a small quantity of water and the diphenylcarbamide which separated was filtered off, the rest being then diluted with several times its volume of water, the milky emulsion filtered from diphenylcarbamide and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid to remove aniline and the ether evaporated; the residue consisted of a pale yellow oil easily identified as benzonitrile.

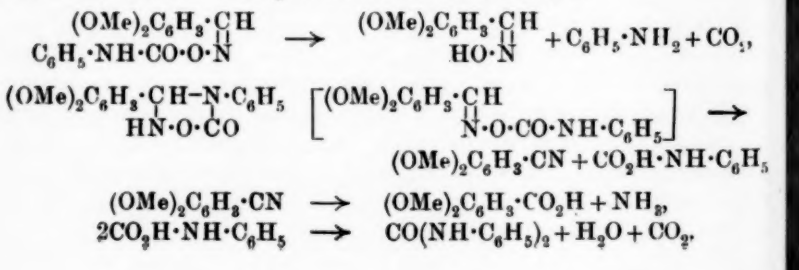
The action of alkalis on carbanilinobenz*syn*aldoxime has been described above. When this compound is kept for some days, it decomposes in a way similar to carbanilino-*m*-nitrobenz*syn*aldoxime, namely, into aniline, benzonitrile, diphenylcarbamide, and carbanilinobenz*anti*aldoxime, which can be separated as in the case of the *m*-nitro-compound.

Beckmann's experiment by which he obtained the compound melting at 94° was repeated. Benz*syn*aldoxime was treated with excess of dry benzene, slightly less than an equimolecular proportion of phenylcarbimide added, and the whole gently warmed until solution was complete. On cooling and evaporating the benzene in a current of dry air, a mass of needle-shaped crystals separated which proved to be carbanilinobenz*anti*aldoxime (m. p. 136°). No trace of the substance melting at 94° was obtained. The conversion of the carbanilinobenz*syn*aldoxime into carbanilinoben*anti*aldoxime was to be expected, as it was necessary to warm the solution.

Various experiments on the recrystallisation of carbanilinobenz*syn*aldoxime from warm solvents, for example, acetone and benzene, gave substances melting at temperatures from 84° to 130° according to the temperature to which the solvent was raised and the time it was kept at that temperature during recrystallisation. Compounds melting in the neighbourhood of 100° were obviously mixtures, and on keeping for some days underwent decomposition similar to all the carbanilino*syn*aldoximes.

Action of Phenylcarbimide on Veratraldoxime.

Equivalent quantities of veratraldoxime and phenylcarbimide in dry ether were mixed in a stoppered bottle, and at the end of thirty minutes a pale yellow oil separated. On shaking and leaving for some time the carbanilino-compound separated on the sides of the vessel in clusters of fine needles. After four hours the solid was removed and pressed on a porous tile; the yellow, crystalline solid so obtained melted at 94° and, after recrystallisation from cold acetone and water, at 104°. This substance exhibited many of the peculiarities of carbanilino-*m*-nitrobenzaldoxime as similarly obtained, recrystallisation sometimes raising and sometimes lowering the melting point. The products of hydrolysis also indicated that it was a mixture. The substance was heated on the water-bath for an hour with 2*N*-sodium hydroxide, when it passed almost completely into solution, and a considerable amount of ammonia was evolved, indicating the formation and hydrolysis of nitrile from the *syn*-derivative present. Aniline could be detected in the solution by the usual tests. The small amount of residue was recrystallised from alcohol and found to be a little unchanged substance and diphenylcarbamide. The alkaline solution was made faintly acid with hydrochloric acid and again made alkaline with sodium carbonate and extracted with ether. On evaporation of the ether an oil remained, which was identified as veratraldoxime by means of its hydrochloride. (It is of interest to note that the method of forming the hydrochloride is often of great use in identifying small quantities of oximes. It is frequently very difficult to induce oximes of low melting point to crystallise, especially if they are not quite pure; if, however, the crude substance is dissolved in dry ether and dry hydrogen chloride passed into the solution, the hydrochloride is precipitated in a pure crystalline form and can be identified, such impurities as acids, aldehydes, and nitriles remaining in solution.) The aqueous sodium carbonate solution was acidified and extracted with ether, the ether removed and evaporated, and the solid obtained was recrystallised from hot water. This proved to be veratric acid.



The mixture described above decomposes on keeping; the *syn*-derivative present disappears, and aniline, diphenylcarbamide, and carbanilinoveratr*anti*aldoxime are the main products. The aniline was removed by washing with dilute hydrochloric acid and the diphenylcarbamide by means of chloroform as described above. The chloroform solution was precipitated with light petroleum, and the substance so obtained, on recrystallisation from alcohol, yielded long, colourless needles of carbanilinoveratr*anti*aldoxime melting at 129°:

0·2352 gave 19·0 c.c. N_2 at 16° and 756 mm. N = 9·5.

$C_{16}H_{16}O_4N_2$ requires N = 9·3 per cent.

Carbanilino-3:4-*dimethoxybenz*syn*aldoxime* appears to be more stable than the corresponding *m*-nitro-compound as it is not possible to convert it into its isomeride by repeated recrystallisations from alcohol. Boiling with alcohol for an hour partly decomposes it, but most of the substance can be recovered and still has the low melting point. If left in contact with the mother liquors, in the preparation of the compound for several days, it is not, like the *m*-nitro-compound, converted almost entirely into the pure *anti*-compound. If the compound of low meltng point is recrystallised from alcohol and the crystals left in contact with the mother liquor for a week, after filtering, one further recrystallisation gives the pure *anti*aldoxime.

Carbanilino-derivatives of the Hydroxybenzaldehydes, $C_6H_5{\cdot}NH{\cdot}CO_2{\cdot}C_6H_4{\cdot}CHO$.

The aldehydes were dissolved in dry ether contained in a stoppered bottle, the requisite quantity of phenylcarbimide added, and the solution allowed to remain for several days.

In the case of *o*-hydroxybenzaldehyde (salicylaldehyde), a small quantity of large, stout crystals formed on the sides of the vessel; these proved to be diphenylcarbamide, formed by the action of traces of moisture on the carbimide, and were removed. The ethereal solution was evaporated in a current of dry air and the solid remaining was washed with a little cold alcohol and recrystallised from benzene, when *o-carbanilino-oxybenzaldehyde* was obtained in colourless needles melting at 133°:

0·1553 gave 7·8 c.c. N_2 at 21° and 752 mm. N = 5·9.

$C_{14}H_{11}O_3N$ requires N = 5·8 per cent.

In the case of the meta- and para-compounds most of the carbanilino-derivative crystallised from the ethereal solution in a state of purity.

m-*Carbanilino-oxybenzaldehyde* crystallises in fine needles melting at 158—160°:

0·2593 gave 12·8 c.c. N_2 at 19° and 763 mm. N = 5·8.

$C_{14}H_{11}O_3N$ requires N = 5·8 per cent.

p-*Carbanilino-oxybenzaldehyde* crystallises in short needles melting at 136°:

0·2571 gave 12·4 c.c. N_2 at 15° and 763 mm. N = 5·7.

$C_{14}H_{11}O_3N$ requires N = 5·8 per cent.

p-Carbanilino-oxybenzaldehyde was boiled with alcohol for several hours under reflux. On cooling the solution, fine needles separated which proved to be diphenylcarbamide. After removing these and diluting the liquid, a crystalline substance separated which was recrystallised and shown to be *p*-hydroxybenzaldehyde. Warming with dilute alkalis decomposes these compounds, aniline and the aldehyde being the products.

p-*Diphenylcarbamyloxybenzaldehyde*, $(C_6H_5)_2N\cdot CO_2\cdot C_6H_4\cdot CHO$.

p-Hydroxybenzaldehyde was dissolved in ether and an equivalent of sodium, dissolved in a minimum of alcohol, was added to the solution. In this way a precipitate of the sodium salt of the aldehyde was obtained. This was collected, dried rapidly on a porous tile, suspended in chloroform, and boiled with an equimolecular proportion of diphenylcarbamyl chloride under reflux for an hour. The mixture was filtered whilst hot from the sodium chloride formed and the chloroform evaporated. The residue was crystallised from alcohol and formed colourless needles melting at 100°, which on keeping, even in the dark, slowly turn blue:

0·2549 gave 10·0 c.c. N_2 at 21° and 763 mm. N = 4·6.

$C_{20}H_{15}O_3N$ requires N = 4·4 per cent.

p-Diphenylcarbamyloxybenzaldehyde was hydrolysed by heating on the steam-bath with 2*N*-alkali for an hour. The solution then had a strong odour of diphenylamine. The small quantity of solid was removed by filtration and found to be unchanged substance. On diluting the filtrate and extracting with ether, diphenylamine was separated and from the aqueous layer, by acidifying and extracting with ether, *p*-hydroxybenzaldehyde was obtained.

$$(C_6H_5)_2N\cdot CO_2\cdot C_6H_4\cdot CHO + H_2O = (C_6H_5)_2NH + CO_2 + HO\cdot C_6H_4\cdot CHO.$$

p-*Diphenylcarbamyloxybenzaldoxime*, $(C_6H_5)_2N\cdot CO_2\cdot C_6H_4\cdot CH{:}N\cdot OH$.

p-Diphenylcarbamyloxybenzaldehyde was dissolved in alcohol and an equivalent of hydroxylamine hydrochloride and rather

less than an equivalent of sodium hydroxide, both dissolved in water, were added to the solution. The mixture was kept in the ice-chest for twenty-four hours, acidified with dilute hydrochloric acid, and the precipitate collected and crystallised from dilute alcohol. The oxime crystallises in large needles melting at 140°:

0·2376 gave 17·2 c.c. N_2 at 18° and 748 mm. N = 8·4.

$C_{20}H_{16}O_3N_2$ requires N = 8·4 per cent.

If an ethereal solution of this compound is saturated with dry hydrogen chloride, an oily hydrochloride is precipitated which, on decomposition with sodium carbonate solution, regenerates the original oxime.

Acetyl-p-*diphenylcarbamyloxybenzaldoxime*, $(C_6H_5)_2N\cdot CO_2\cdot C_6H_4\cdot CH{:}N\cdot CO_2\cdot CH_3$.

p-Diphenylcarbamyloxybenzaldoxime was dissolved in warm acetic anhydride and the excess of the reagent decomposed with sodium carbonate solution. The solid so obtained was recrystallised from alcohol, when the acetyl derivative separated in fine crystals melting at 134°:

0·2137 gave 14·4 c.c. N_2 at 20° and 748 mm. N = 7·7.

$C_{21}H_{18}O_4N_2$ requires N = 7·5 per cent.

p-Diphenylcarbamyloxybenzaldoxime and its acetyl derivative were hydrolysed by boiling with 2*N*-sodium hydroxide for five minutes. At the end of that time the solutions were cooled, diluted and extracted with ether to remove diphenylamine; on acidifying the aqueous layer and again extracting with ether, *p*-hydroxybenzaldoxime was obtained in each case.

Dicarbanilino-m- *and* -p-*oxybenzaldoximes*, $C_6H_5\cdot NH\cdot CO_2\cdot C_6H_4\cdot CH{:}N\cdot CO_2\cdot NH\cdot C_6H_5$.

In each case the oximes were dissolved in ether and two equivalents of phenylcarbimide added. After some days the ether was removed and the residue recrystallised from alcohol.

The meta-compound crystallises in colourless prisms melting at 158—160°:

0·2096 gave 20·0 c.c. N_2 at 15° and 748 mm. N = 11·2.

The para-compound forms colourless crystals melting at 145°:

0·2058 gave 20·0 c.c. N_2 at 15° and 761 mm. N = 11·5.

$C_{21}H_{17}O_4N_3$ requires N = 11·2 per cent.

These compounds, on hydrolysis, yield aniline and the corresponding hydroxybenzaldoxime.

Diphenylcarbamyl-p-*diphenylcarbamyloxybenzaldoxime*, $(C_6H_5)_2N\cdot CO_2\cdot C_6H_4\cdot CH{:}N\cdot CO_2\cdot N(C_6H_5)_2$.

p-Hydroxybenzaldoxime was dissolved in alcohol and two equivalents of sodium dissolved in alcohol were added. The solution was then boiled with two equivalents of diphenylcarbamyl chloride for thirty minutes. The hot solution was filtered from sodium chloride and crystallised on cooling. The compound was recrystallised from alcohol, when colourless crystals, melting at 162°, were obtained:

0·1708 gave 11·8 c.c. N_2 at 17° and 750 mm. N = 8·0.
$C_{33}H_{25}O_4N_3$ requires N = 8·0 per cent.

Carbethoxy-p-*nitrobenz*syn*aldoxime*, $NO_2\cdot C_6H_4\cdot CH{:}NO\cdot CO_2\cdot C_2H_5$.

p-Nitrobenz*anti*aldoxime was dissolved in a slight excess of sodium hydroxide solution, a slight excess of ethyl chlorocarbonate added and the mixture shaken thoroughly, keeping it as cool as possible. The solid which separated was collected and crystallised from warm alcohol. In this way *carbethoxy*-p-*nitrobenz*syn*aldoxime* is obtained in pale yellow needles melting at 94°:

0·1804 gave 18·4 c.c. N_2 at 17° and 760 mm. N = 12·0.
$C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.

This compound was hydrolysed by boiling with 2*N*-sodium hydroxide for an hour; ammonia was evolved, and on acidifying, the precipitate obtained was almost completely soluble in sodium carbonate solution, and was found to be almost pure *p*-nitrobenzoic acid (m. p. 238°):

$$NO_2\cdot C_6H_4\cdot \underset{\displaystyle NO\cdot CO_2\cdot C_2H_5}{\overset{\displaystyle \|}{C}}H \longrightarrow NO_2\cdot C_6H_4\cdot CN + CO_2 + C_2H_5\cdot OH$$

$$NO_2\cdot C_6H_4\cdot CN + 2H_2O \longrightarrow NO_2\cdot C_6H_4\cdot CO_2H + NH_3.$$

Carbethoxy-p-*nitrobenz*anti*aldoxime*.—If carbethoxy-*p*-nitrobenz-*syn*aldoxime is boiled with alcohol for a short time or twice recrystallised from boiling alcohol, long needles, melting at 109°, separate, consisting of *carbethoxy*-p-*nitrobenz*anti*aldoxime*:

0·3518 gave 35·6 c.c. N_2 at 17° and 760 mm. N = 11·9.
$C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.

If this compound is boiled with 2*N*-sodium hydroxide, ammonia is not evolved, and on acidifying the solution the precipitate is not soluble in sodium carbonate solution; after recrystallisation it melts at 128°, and when mixed with *p*-nitrobenz*anti*aldoxime (m. p. 129°) at 129°:

$$NO_2\cdot C_6H_4\cdot \underset{\displaystyle C_2H_5\cdot CO_2\cdot O\cdot N}{\overset{\displaystyle \|}{C}}H + H_2O \longrightarrow NO_2\cdot C_6H_4\cdot \underset{\displaystyle HO\cdot N}{\overset{\displaystyle \|}{C}}H + CO_2 + C_2H_5\cdot OH.$$

Carbethoxy-m-*nitrobenz*anti*aldoxime and Carbethoxy*-p-*dimethylaminobenz*anti*aldoxime.*

These compounds were prepared by dissolving the oxime in a slight excess of sodium hydroxide and shaking with ethyl chlorocarbonate. The product in each case proved to be the carbethoxy-*anti*aldoxime giving, on hydrolysis, the original oxime. In spite of all precautions to avoid isomeric change during the preparation, it has not been possible so far to isolate the *syn*-isomeride, as in the case of the *p*-nitro-compound.

Carbethoxy-m-*nitrobenz*anti*aldoxime* crystallises from alcohol in colourless laminæ melting at 97°:

0·1652 gave 17·0 c.c. N_2 at 17° and 760 mm. N = 12·1.
$C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.

Carbethoxy-p-*dimethylaminobenz*anti*aldoxime* crystallises from alcohol in colourless, shining plates, melting at 118°, which slowly turn pale green:

0·1573 gave 15·8 c.c. N_2 at 16° and 756 mm. N = 11·8.
$C_{12}H_{16}O_3N_2$ requires N = 11·9 per cent.

Action of Liquid Hydrogen Chloride on Certain Oximes.

If benz*anti*aldoxime, in small quantities at a time, is added to liquid hydrogen chloride, the reaction mixture allowed slowly to attain the ordinary temperature, and the solid residue pressed on a porous plate, a granular compound (m. p. 105°) is obtained identical with the hydrochloride obtained by Luxmoore (*loc. cit.*) by saturating an ethereal solution of benz*anti*aldoxime, cooled to 0°, with hydrogen chloride. This hydrochloride, like Luxmoore's, on decomposition with sodium carbonate solution, always gave an oil. This was removed with ether, the solvent evaporated in a current of dry air, and the oil kept overnight in a vacuum over sodium hydroxide, when a small quantity of benz*syn*aldoxime crystallised out. The main bulk of the product was, however, benz-*anti*aldoxime. This hydrochloride, on recrystallisation, changes to the hydrochloride melting at 63°, which, with sodium carbonate solution, gives a solid consisting of benz*syn*aldoxime.

If benz*syn*aldoxime is treated with liquid hydrogen chloride in the same way a compound melting at 103° is obtained:

0·1034 requires 6·4 c.c. $N/10$-$AgNO_3$. Cl = 22·0.
C_7H_8ONCl requires Cl = 22·5 per cent.

This differs from the hydrochloride described above in that, on

decomposition with sodium carbonate solution, it always yields a solid which consists mainly of benz*syn*aldoxime. These experiments have been repeated several times and always with the same results.

Similar experiments have been undertaken with *p*-nitrobenzaldoxime, but with less definite results. *p*-Nitrobenz*anti*aldoxime dissolves in liquid hydrogen chloride to give an orange solution; if the excess of hydrogen chloride is allowed to evaporate, an oily substance is obtained, which soon sets to a solid, and proves to be a hydrochloride melting at 123°. This hydrochloride, on decomposition with sodium carbonate solution, gives a crude oxime sintering at 118° and melting at 135°. If this crude substance is recrystallised from acetone and water, and only a small fraction separated, *p*-nitrobenz*syn*aldoxime (m. p. 170°) is obtained. The crude substance is obviously a mixture of the *syn*- and *anti*-isomerides.

The hydrochloride obtained in the usual way also gives a mixture of the two isomerides, although a greater quantity of the *syn*-compound is formed, the crude substance usually melting in the neighbourhood of 145° and sintering at but a few degrees lower.

If, instead of allowing the liquid hydrogen choride to evaporate in the above experiment, the mixture is poured into a large excess of sodium carbonate solution, the crude oxime melts at 103°, and after recrystallisation at 132°, and only after a further recrystallisation at 143°. If *p*-nitrobenz*syn*aldoxime is treated with liquid hydrogen chloride, the solid does not dissolve and the liquid remains almost colourless. The hydrochloride obtained on allowing the hydrogen chloride to evaporate melts at 126°, and, on decomposition with sodium carbonate solution, gives a crude oxime melting at 145°.

These results seem to indicate that the amount of *syn*-forming hydrochloride given by the *anti*-oxime is decreased at low temperatures, *p*-nitrobenzaldoxime thus resembling, to some extent, benzaldoxime.

It may be pointed out that the formation of the hydrochloride of benz*anti*aldoxime takes place at higher temperatures than 0°, a considerable amount of this compound being formed at 10—12°. The authors at one time had considerable trouble in preparing quantities of benz*syn*aldoxime during some cold weather, the product being always contaminated with much benz*anti*aldoxime. It was eventually discovered that the difficulty arose from the low temperature of the ethereal solution of the benz*anti*aldoxime, as no difficulty was encountered if the solution was warmed to 20° preparatory to passing in the hydrogen chloride.

In conclusion, the authors wish to express their thanks to the Research Fund Committee of the Chemical Society for grants which have defrayed the expenses of this work.

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LV.—*Reactivity of the Halogens in Organic Compounds. Part IX. Interaction of Alkalis and Alkali Bromoacetates and Bromopropionates in Ethyl-alcoholic Solution.*

By GEORGE SENTER and HENRY WOOD.

IN a previous paper (T., 1915, **107**, 1070), the action of alkalis on alkali bromoacetates and bromopropionates respectively in methyl alcohol and in mixtures of methyl alcohol and water was discussed, and it was shown that Madsen's conclusions (T., 1913, **107**, 965) as to the order of the reactions required modification in certain important respects. In agreement with Madsen, it was found that in mixtures of methyl alcohol and water both hydroxy-acids and alkyloxy-acids are formed, as was to be expected from the fact that in the mixed solvent an equilibrium is established represented by the equation:

$$CH_3{\cdot}ONa + H_2O \rightleftharpoons CH_3{\cdot}OH + NaOH,$$

and that sodium methoxide and sodium hydroxide act simultaneously on the alkali salt of the bromo-acid, forming salts of the hydroxy-acid and alkyloxy-acid respectively. A remarkable feature of the reactions is that under equivalent conditions a much larger proportion of alkyloxy-acid than of hydroxy-acid is formed. The simplest explanation of these observations is that when water and methyl alcohol are present in equivalent proportions the amount of sodium methoxide present is greater than that of sodium hydroxide (compare Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 41, 311).

In the present paper, the results of a corresponding investigation with solutions in ethyl alcohol and in mixtures of ethyl alcohol and water are described. As already pointed out (*loc. cit.*, p. 1080), sodium bromoacetate is only sparingly soluble in ethyl alcohol, and it was therefore impossible to measure the speed of the reaction between sodium bromoacetate and sodium ethoxide. A series of

measurements in mixtures of ethyl alcohol and water in various proportions shows that the rate of displacement of bromine increases with increasing proportion of alcohol, so far as the measurements could be carried. The reaction, as in methyl alcohol, is pseudo-bimolecular in character; in any one solution velocity coefficients in good agreement with the assumption that the reaction is bimolecular are obtained, but with different initial concentrations of the reacting substances, the velocity coefficients increase faster than the concentration of the sodium ethoxide. It is remarkable that the bromine is displaced about six times as fast in 90 per cent. ethyl alcohol as in 90 per cent. methyl alcohol. The proportion of ethoxy-acid in the final product was estimated by Zeisel's method, and it was found that in solutions containing up to 40 per cent. alcohol the proportion of ethoxy-acid formed is greater than that of the alcohol present in the solution.

The action of ethyl alcohol on sodium bromopropionate is comparable in speed with that of sodium ethoxide, so that the reaction does not correspond with any simple order. The rate of displacement of bromine attains a maximum in mixtures containing about 25 per cent. ethyl alcohol.

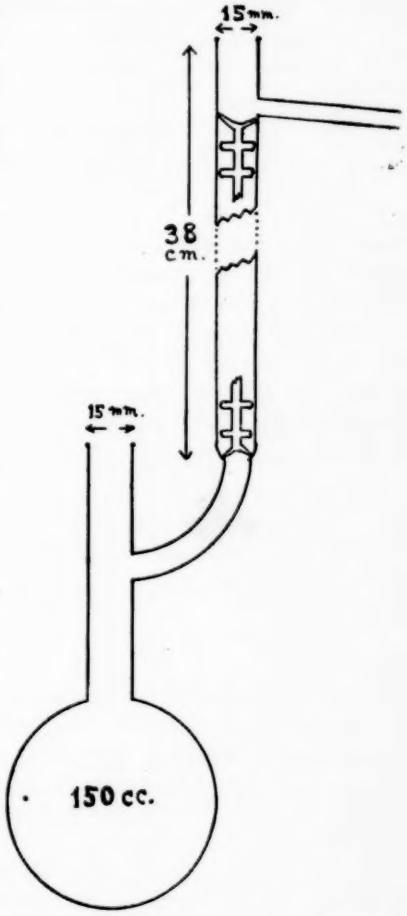
The bearing of the results summarised in the last two paragraphs is briefly discussed in later sections of the paper.

Experimental.

The method of experiment has been fully described in the previous paper, as well as the tests used in establishing the purity of the materials. The results were calculated by the usual formula for a bimolecular reaction, $a-x$ representing the number of c.c. of approximately $N/10$-sulphuric acid required to neutralise 20 c.c. of the reaction mixture after the latter had been heated for a definite period at constant temperature. The titration value at the time, $t=0$, is not that at the commencement of the reaction, but a measurement made after the mixture had been so long in the thermostat that the temperature was assumed to have become constant.

For estimating the proportion of ethoxyl present by Zeisel's method, a slight modification of Hewitt and Moore's apparatus (T., 1902, **81**, 318) suggested by one of us (H. Wood) was found to give excellent results. The modification consists in using as decomposition vessel a flask with a side-tube, into which the fractionating column is inserted. By this arrangement, only singly bored corks are used, and complete tightness is easily secured. The arrangement will be clear from the diagram without further description.

The hydriodic acid used in the Zeisel determinations was purified by adding a little red phosphorus and heating for three to four hours on a water-bath in an atmosphere of carbon dioxide, in a flask provided with an air condenser. The liquid was then allowed to cool while a slow stream of carbon dioxide was maintained, and then filtered through an asbestos plug under pressure of carbon dioxide from a Kipp's apparatus.



Reaction between Sodium Bromoacetate and Ethoxide in Mixtures of Ethyl Alcohol and Water.

This reaction is represented quantitatively by the equation:

$$CH_2Br\cdot CO_2Na + C_2H_5\cdot ONa \longrightarrow C_2H_5\cdot O\cdot CH_2\cdot CO_2Na + NaBr.$$

As already mentioned, it was not found possible to determine the rate of reaction between sodium bromoacetate and sodium ethoxide in ethyl alcohol alone, owing to the sparing solubility of the salt in this solvent. Measurements were made using as solvent mixtures containing varying proportions of ethyl alcohol and water. The results of typical experiments in 90 per cent. and 50 per cent. alcohol by volume are given in the accompanying table.

TABLE I.

Sodium Bromoaceate, 0·1*N*.
Sodium Ethoxide, 0·1*N*.

90 per cent. Alcohol.			50 per cent. Alcohol.		
t.	*a* − *x*.	*k*.	*t*.	*a* − *x*.	*k*.
0	16·95	—	0	19·7	—
30	13·45	0·00050	30	18·25	0·000134
60	11·1	0·00052	60	17·1	0·000129
120	8·3	0·00051	120	15·1	0·000129
180	6·5	0·00052	185	13·4	0·000129

As the figures given in the third and sixth columns show, the reaction is strictly bimolecular in these dilutions, and this was also found to be the case in all the mixtures used as solvent. This is a remarkable result when account is taken of the marked alteration in the nature of the solvent, ranging from pure water to 90 per cent. alcohol. The velocity coefficients for different initial concentrations of sodium ethoxide in 90 per cent. alcohol are given in Table II. The temperature throughout was 40·2°.

TABLE II.

Sodium ethoxide.	Sodium bromoacetate.	$k \times 10^3$.
0·1 *N*	0·1*N*	0·51
0·15*N*	0·1*N*	0·57
0·2 *N*	0·1*N*	0·76
0·3 *N*	0·1*N*	0·82

If the rate of reaction is proportional to the concentration of the sodium salt (ethoxide and hydroxide) the coefficients in the last column should be the same, whereas they are greater the greater the concentration of the sodium salt. As this result might possibly be due to the greater reactivity of non-ionised sodium ethoxide, which is present in relatively larger proportion than the C_2H_5O' ion in the more concentrated solutions, the effect of sodium bromide, which increases the proportion of non-ionised salt, was examined. In *N*/10-solution of the bromoacetate and ethoxide with 0·2*N*-sodium bromide, the velocity coefficient is 0·00084, whereas in the absence of the latter salt, the coefficient is 0·00051. The interpretation of this result is discussed later (p. 686).

The velocity coefficient with *N*/10-potassium ethoxide in 90 per cent. alcohol is 0·00056, as compared with 0·00051 for the sodium salt under equivalent conditions, so that in this case also the potassium salt is slightly more reactive (compare T., 1915, **107**, 1074).

It has already been mentioned that the proportion of ethoxy-

acid in the products of the reaction was determined for mixtures containing varying proportions of alcohol. The results of these determinations, together with the velocity coefficients in the various mixtures, are given in the accompanying table.

TABLE III.

Sodium Bromoacetate, N/10.
Sodium Ethoxide (Hydroxide), N/10.

Proportion of Alcohol by volume	100	90	75	50	25	10	0 (NaOH only)
Velocity Coefficient $\times 10^3$ ...	—	0·51	0·24	0·13	0·10	—	0·082
Proportion of Ethoxy-acid in product	90·8	81·6	69·0	48·0	31·0	14·3	—

These results show that the rate of displacement of bromine increases regularly as the proportion of alcohol increases, and that, at least in the more dilute solutions, the proportion of ethoxy-acid formed is greater than the proportion of ethyl alcohol present.

The reason why the proportion of ethoxy-acid is less than 100 per cent. in alcohol alone has not been satisfactorily elucidated. As already mentioned, the bromoacetate is only sparingly soluble in ethyl alcohol at 40°, and the mixture had to be heated either at a much higher temperature to complete the decomposition of the bromoacetate, or at the lower temperature in presence of undissolved salt, so that a secondary product of some character was probably formed in small amount.

The velocity coefficient for the action between sodium bromoacetate and sodium methoxide in 90 per cent. methyl alcohol is $0{\cdot}30 \times 10^{-3}$ at 52·4°, and as the temperature coefficient for 10° for this reaction is 2·8, the coefficient at 40·2° would be about $0{\cdot}08 \times 10^{-3}$, which is about one-sixth of the rate of the corresponding reaction in ethyl alcohol. The relatively great velocity of the reaction between sodium ethoxide and sodium bromoacetate doubtless accounts for the regular increase in the velocity coefficients as the proportion of alcohol is increased (Table III).

The greater reactivity of sodium ethoxide as compared with sodium methoxide has been observed for other reactions. Thus, according to Hecht and Conrad (*Zeitsch. physikal. Chem.*, 1889, **4**, 299), sodium ethoxide reacts with ethyl iodide about four times as fast as does sodium methoxide, and Kremann (*Monatsh.*, 1905, **26**, 279) found that the rate of hydrolysis of ethyl acetate by sodium ethoxide in ethyl alcohol is about 1·4 times as great as

the corresponding reaction with sodium methoxide in methyl alcohol. Kremann was of opinion that this result is to be ascribed to the influence of traces of moisture in the alcohols, which would form a much greater proportion of sodium hydroxide from sodium ethoxide than from sodium methoxide; as sodium hydroxide hydrolyses ethyl acetate several hundred times faster than the alkyloxide, the observed results would thus be accounted for. In this connexion, it is interesting to note that the solvent used in the classical experiments of Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1899, **3**, 450; **4**, 272, 631; 1890, **5**, 289) was 99·8 per cent. alcohol. In the experiments described in this paper, however, as hydroxyl ions act relatively slowly on sodium bromoacetate, the explanation for the relatively great reactivity of sodium ethoxide suggested by Kremann cannot apply, and it is doubtful if the small proportion of water present in Hecht and Conrad's experiments had much effect on the character of the results. In fact, it would probably be found, contrary to the opinion of Kremann, that in the entire absence of water sodium ethoxide would react with ethyl acetate more rapidly than would sodium methoxide.

It is not easy to suggest a satisfactory explanation for the relatively great reactivity of sodium ethoxide. Reactions in methyl alcohol will usually be more rapid than in ethyl alcohol, owing to the higher dielectric constant and smaller viscosity of the former solvent (Menschutkin), so that the true ratio of the chemical activity of sodium ethoxide to methoxide, determined in the same solvent, would probably be greater than the value given above. So far as steric hindrance is concerned, the methoxide might be expected to react more rapidly than the ethoxide. It may be that the methoxy-group takes up more affinity from the sodium than the ethoxy-group, and therefore the sodium atom united with the latter group, having more affinity left over, is able to displace the bromine more rapidly than that attached to the methoxy-group. The effect of sodium bromide in accelerating the action would appear to show that the non-ionised alkyloxide, and not the anion, is the main factor in the change.

As far as the relative proportions of ethoxy-acid obtained from the solvents containing different proportions of alcohol and water are concerned, there is little to add to the discussion in the previous paper (*loc. cit.*, p. 1078). It is there pointed out (p. 1078) that, in drawing conclusions as to the relative proportions of hydroxide and alkyloxide in the mixture from the relative proportions of hydroxy-acid and alkyloxy-acid in the final product, the relative rates of reaction of hydroxide and alkyloxide with the bromo-acid

have to be taken into account. The results now given show, as was to be anticipated, that the equilibrium

$$C_2H_5\cdot ONa + H_2O \rightleftharpoons C_2H_5\cdot OH + NaOH$$

is displaced more to the right than in solutions of sodium methoxide under equivalent conditions. The observations cannot be interpreted quantitatively until the above equilibrium has been more accurately investigated, especially by means of electrical conductivity measurements. The suggestion of Kremann (*loc. cit.*) that the proportion of alkyloxide in such mixtures containing 50 per cent. of water is extremely small is not borne out by his own observations, owing to the relatively great effect of even a small proportion of sodium hydroxide on the rate of hydrolysis of ethyl acetate, and is disproved by the results described in the present paper.

Reaction between Sodium Bromopropionate and Ethoxide in Ethyl Alcohol and in Mixtures of Ethyl Alcohol and Water.

As sodium bromopropionate is fairly soluble in ethyl alcohol, it was possible to determine the speed of this reaction in 100 per cent. alcohol, as well as in mixtures of ethyl alcohol and water. As the reaction is much slower than in the case of sodium bromoacetate, the measurements were carried out at 51·4°. The results of typical experiments in 90 and 50 per cent. alcohol are given in Table IV.

TABLE IV.

Sodium α-Bromopropionate, N/10.
Sodium Ethoxide, N/10.

90 per cent. Alcohol.			50 per cent. Alcohol.		
t.	$a-x$.	$k \times 10^3$	*t.*	$a-x$.	$k \times 10^3$
0	20·1	—	0	19·75	—
60	18·4	0·076	60	17·75	0·095
120	16·7	0·084	120	16·0	0·099
240	14·1	0·088	240	13·3	0·102
360	12·3	0·088	360	11·2	0·107
480	10·65	0·092	480	9·2	0·121

As the coefficients increase regularly as the reaction proceeds, it is evident that the assumption that the reaction is bimolecular in character is not justified. As a similar result in the case of solutions in methyl alcohol was shown to be due to the fact that the action of sodium methoxide and methyl alcohol on sodium bromopropionate are comparable in speed, the action of ethyl alcohol

on sodium bromopropionate was investigated. The main reaction is presumably that represented by the equation

$$CH_3{\cdot}CHBr{\cdot}CO_2Na + C_2H_5{\cdot}OH \longrightarrow CH_3{\cdot}CH(O{\cdot}C_2H_5){\cdot}CO_2H + NaBr.$$

As it has been found in previous investigations that the rate of formation of bromidion is not always the same as the rate of increase of the acidity of the solution, as would be the case if the above equation adequately represented the course of the reaction, the speed of the change was followed by titrating the solution with $N/10$-silver nitrate, as well as with $N/10$-sodium hydroxide. The results of a typical experiment at 51·4° are given in the accompanying table. The velocity coefficients, k, have been calculated for the silver nitrate titrations only by the formula for a unimolecular reaction.

TABLE V.

Sodium α-Bromopropionate, N/10, in Ethyl Alcohol.

t.	c.c. $N/10$-$AgNO_3$.	c.c. $N/10$-NaOH.	$a-x'$.	$a-x''$.	$k \times 10^3$.
0	0·2	0·2	19·8	19·8	—
60	1·1	0·85	18·9	19·15	0·944
180	2·6	2·00	17·4	18·0	0·774
300	3·85	2·95	16·15	17·05	0·712
510	5·55	4·2	14·45	15·8	0·638
1680	11·1	8·25	8·9	11·75	0·482

When the coefficients in column 6 are divided by 20, to make them comparable with those in table IV, the conclusion that ethyl alcohol and sodium ethoxide act on sodium α-bromopropionate at comparable rates is confirmed.

As shown in the last paper (*loc. cit.*, p. 1075; compare *Ber.*, 1912, **45**, 2318), the difference in the titration values with silver nitrate and sodium hydroxide is due to the intermediate formation of the compound

$$CH_3{\cdot}CH(O{\cdot}CO{\cdot}CHBr{\cdot}CH_3){\cdot}CO_2Na$$

by the interaction of two molecules of sodium α-bromopropionate. This compound would undergo slow decomposition by ethyl alcohol with the formation of bromopropionic acid and α-ethoxypropionic acid, and the fact that the simultaneous titration values with silver nitrate and sodium hydroxide differ more in ethyl- than in methyl-alcoholic solution doubtless indicates that the intermediate compound is decomposed more rapidly by methyl than by ethyl alcohol. α-Chloroacetoxypropionic acid,

$$CH_3{\cdot}CH(O{\cdot}CO{\cdot}CH_2Cl){\cdot}CO_2H,$$

similar in constitution to the above compound, has been prepared in this laboratory by Mr. G. H. Martin by a method described by Blaise (*Bull. Soc. chim.*, 1914, [iv], **15**, 666), and it is intended

at a later stage to give an account of the behaviour of such compounds from the kinetic point of view.

The rapid diminution in the magnitude of the velocity coefficients calculated for a unimolecular reaction is doubtless to be ascribed to the formation of hydrobromic acid during the reaction, whereby the sodium salt is changed to free bromopropionic acid, which reacts more slowly than the salt. Towards the end of the reaction the odour of ethyl α-bromopropionate becomes perceptible.

The relative rates of reaction of sodium methoxide and ethoxide with sodium bromopropionate cannot be determined with any degree of accuracy, as the results are complicated by the action of the alcohols themselves on the salt.

As already mentioned, the rate of displacement of bromine from sodium α-bromopropionate has also been investigated in mixtures of ethyl alcohol and water. The approximate values of the velocity coefficients at different dilutions, calculated by the formula for a bimolecular reaction, are given in table VI.

TABLE VI.

Sodium α-Bromopropionate, 0·1*N*.
Sodium Ethoxide (*Hydroxide*), 0·1*N*.

Proportion of Ethyl Alcohol by volume	100	90	75	50	25	10	0 (NaOH only)
Velocity Coefficient × 10^3 ...	0·113	0·087	0·098	0·107	0·130	0·115	0·097

It is interesting to note that there is a maximum rate of reaction in the solution containing 25 per cent. by volume of alcohol. As the results given in the present and in previous papers show that the change is a highly complicated one, at least four simultaneous reactions taking place, namely, the action of ethyl alcohol, sodium ethoxide, water, and sodium hydroxide respectively on sodium bromopropionate, there is no advantage in discussing the results more fully at the present stage.

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[*Received, June 14th*, 1916.]

LVI.—*Studies on the Walden Inversion. Part III. The Kinetics and Dissociation Constant of Phenylbromoacetic Acid.*

By George Senter and Stanley Horwood Tucker.

Within the last two or three years it has been discovered that a Walden inversion may be brought about by slighter alterations of the experimental conditions than those made familiar by the earlier work on the subject. Thus Senter and Drew (T., 1915, **107**, 638, and a second communication shortly to be published) have shown that optically active products of opposite sign may be obtained when the same reaction—the formation of phenylaminoacetic acid from phenylchloroacetic acid—is carried out in different solvents, and Holmberg (*Ber.*, 1914, **47**, 176), by the action of potassium and strontium xanthates under different experimental conditions on *l*-bromosuccinic acid, has obtained solutions from which products consisting mainly of *d*- or of *l*-xanthosuccinic acid have been isolated.

The simplest possible case of a Walden inversion would be the formation of products of opposite sign by the action of water alone (or any other solvent) on an optically active compound under varying experimental conditions (compare McKenzie and Walker, T., 1915, **107**, 1685). The possibility of this was first opened up by the discovery by one of us (Senter, T., 1909, **95**, 1836) that when α-bromopropionic acid is hydroxylated in aqueous solution, the non-ionised acid and the $CHMeBr{\cdot}CO_2'$ ion are simultaneously acted on to form α-hydroxypropionic acid. In concentrated solution the reaction proceeds mainly by hydroxylation of the non-ionised acid and in dilute solution by hydroxylation of the anion. If the ion and the non-ionised acid yield products of opposite sign—and such cases are almost certain to occur—a Walden inversion could be accomplished simply by varying the dilution. No instance of this is yet known, but the discovery of such is presumably only a matter of further investigation. We hope to examine the hydroxylation of α-bromopropionic acid and allied compounds from this point of view as soon as opportunity permits.

The present communication deals with the chemical kinetics of the displacement of bromine by hydroxyl in *r*-phenylbromoacetic acid and sodium phenylbromoacetate. A convenient method for the resolution of this acid has recently been described by McKenzie and Walker (*loc. cit.*). They find that when the free, active acid

is acted on by water, extensive racemisation occurs, but the resulting mandelic acid is slightly active and of the opposite sign to the bromo-acid taken; it thus corresponds with the behaviour of phenylchloroacetic acid. When, however, the sodium salt is hydroxylated in the presence of water or alkali, the product is completely inactive. The authors state that when the *l*-acid is acted on by water, the solution is still very slightly lævorotatory after all the bromine has been displaced, and later becomes slightly dextrorotatory; a possible explanation of this remarkable behaviour is suggested.

It was recently shown (Senter, T., 1915, **107**, 908) that when phenylchloroacetic acid is acted on by water, and the sodium salt is acted on by water and by alkali, with formation of the corresponding hydroxy-acid, the mechanism of the three apparently different reactions is in reality identical, namely, the action of non-ionised water on the $CHPhCl{\cdot}CO_2'$ ion. The observation of McKenzie and Clough (T., 1908, **93**, 811) that a mandelic acid of the same sign was obtained from the three solutions was thus satisfactorily explained. The results for the bromo-acid show, as was to be expected, a close analogy to those for the chloro-acid. The displacement of bromine in the sodium salt in aqueous and in alkaline solution is brought about by the action of water on the $CHPhBr{\cdot}CO_2'$ ion, and this is also the main reaction when water acts on the free acid. In the presence of hydrobromic acid, however, the action of water on the non-ionised acid becomes of importance. Owing to the sparing solubility of the acid in water, only dilute solutions can be examined, and as the concentration of the hydrobromic acid formed in the course of the reaction is thus necessarily small, the action of water alone on the bromo-acid is almost exclusively determined by the action of water on the anion. The conclusion may therefore be drawn that when optically active phenylbromoacetic acid is acted on by water, and the sodium salt is acted on by water and by alkali, the products should be of the same sign. Unfortunately, as already mentioned, this conclusion apparently cannot be tested owing to the fact that the mandelic acid obtained from the sodium salt is completely racemised when the reaction proceeds at room temperature, although there remains the possibility of obtaining a slightly active product by working at a lower temperature. On account of its great tendency to racemisation and its slight solubility in water, this acid also proves unsuitable for testing the conclusion deduced from previous kinetic measurements, as mentioned above, that it should be possible to obtain products of different sign by the action of water alone on an optically active compound.

One of the main objects of our work with phenylbromoacetic acid is to investigate the influence of the solvent on the sign of the product when bromine is displaced from the optically active acid, as has already been done by Drew and one of us for phenylchloroacetic acid (*loc. cit.*). This work is now in progress.

For the interpretation of the kinetic measurements, a knowledge of the extent to which phenylbromoacetic acid is ionised in aqueous solution is required. The dissociation constant of this acid has not hitherto been determined, doubtless because the conductivity changes fairly rapidly in solution owing to progressive hydroxylation.

Dissociation Constants of Phenylbromoacetic and Phenylchloroacetic Acids.

For the determination of the dissociation constant of phenylbromoacetic acid the electrical conductivity method was used, the measurements being made in the ordinary way with a Wheatstone bridge and telephone. The water used in making up the solutions had in no case a conductivity exceeding $1{\cdot}2 \times 10^{-6}$ mhos. at 25°. As the conductivity of the solutions altered fairly rapidly on keeping, measurements were made at definite intervals of time after preparing the solutions, and the initial conductivity was obtained by extrapolation. An additional difficulty in the measurements was that the acid dissolved very slowly in water, and in the more concentrated solutions at least ten minutes elapsed after adding the acid to the water before the first measurements could be taken. The results in the table are the mean of several independent series of measurements. The temperature was 25±0·02°.

TABLE I.

Dilution, v. (Litres per mol.)	κ.	Λ.	α.	$K=\alpha^2/(1-\alpha)v$.
100	0·001671	167·1	0·443	0·00353
200	0·001035	207·0	0·550	0·00336
500	0·000538	269·0	0·714	0·00356
1000	0·000307	307·5	0·815	0·00358
2000	0·000168	336·0	0·891	0·00364

In order to calculate the dissociation constant from the conductivity of the acid, the equivalent conductivity of the latter at infinite dilution, Λ_∞, is required. This is obtained by adding together the value for $H^{\cdot}$, which may be taken as 347·0 at 25°, and that for the $CHPhBr{\cdot}CO_2'$ ion. The usual method of determining the latter value would be to determine Λ_∞ for the sodium salt, but such measurements in the present case would be liable

to considerable inaccuracy owing to the rapid hydroxylation of the salt. As Λ_∞ for the $CHPhCl{\cdot}CO_2'$ ion was found to be 30, it is certain that no substantial error will be committed by assuming the same value for the $CHPhBr{\cdot}CO_2'$ ion. The value of Λ_∞ for phenylbromoacetic acid is therefore 377, and the values of α and K in the table are calculated with this number. Considering the difficulty of the measurements, the values at different dilutions are in good agreement, and the dissociation constant of phenylbromoacetic acid at 25° may be taken as 0·0035 when concentrations are expressed in mols. per litre.

After the additional experience gained in working with substances the conductivity of which alters as measurements are being made, it was decided to repeat the determination of the dissociation constant of phenylchloroacetic acid. The results are in good agreement with those previously obtained (*loc. cit.*), but the mean value of K is slightly lower. The new values of the specific conductivity, κ, at different dilutions and of the dissociation constant calculated from them are as follows:

TABLE II.

Concentration.	$N/50$.	$N/100$.	$N/200$.	$N/500$.	$N/1000$
$\kappa \times 10^2$	0·2795	0·1795	0·1123	0·0557	0·0315
$K \times 10^2$	0·437	0·432	0·439	0·421	0·425

The mean value is 0·0043, whilst the value previously found was 0·0046. Combining the two results, and giving more weight to the later series, the value of K for phenylchloroacetic acid may be taken as 0·0044. The slightly lower value of K does not alter in any respect the conclusions of the previous paper (compare p. 695).

The Hydroxylation of Phenylbromoacetic Acid.

The reaction between phenylbromoacetic acid and water is represented quantitatively by the equation

$$C_6H_5{\cdot}CHBr{\cdot}CO_2H + H_2O \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CO_2H + HBr.$$

As the acid is ionised to a considerable extent in aqueous solution, one of the main objects of the investigation was to determine whether the non-ionised acid or the anion is the main factor in the change. Much light is thrown on this subject by the effect of hydrobromic acid on the rate of the reaction. The results of typical experiments at 25·0° and 40·4°, with and without hydrobromic acid, are given in table III. With the small concentrations of hydrobromic acid employed the back reaction is quite

negligible, and the reaction may therefore be regarded as proceeding completely from left to right.

As already mentioned, phenylbromoacetic acid is only sparingly soluble in water, and solutions more concentrated than $N/40$ could not be used. Even in this dilution, action had progressed some distance before solution was complete. The numbers under $a-x$ represent the concentrations of the unaltered phenylbromoacetic acid at the times t. The time $t=0$ is that at which the first titration was taken.

TABLE III.

Phenylbromoacetic Acid, $N/40$.

No HBr; temperature, 25·0°.

t.	$a-x$.	k.
0	8·5	—
30	7·35	0·00484
60	6·5	0·00447
120	5·2	0·00410
180	4·2	0·00392
270	3·1	0·00374

No HBr; temperature, 40·4°.

t.	$a-x$.	k.
0	3·75	—
10	2·50	0·0405
20	1·85	0·0352
35	1·25	0·0314
55	0·75	0·0293
95	0·30	0·0235

No HBr; temperature, 25·0°.

t (min.).	$a-x$.	k.
0	9·5	—
180	8·7	0·00049
300	8·1	0·00053
420	7·7	0·00050
1320	4·9	0·00050
1900	4·0	0·00046
2985	2·5	0·00045

No HBr; temperature, 40·4°.

t (min.).	$a-x$.	k.
0	8·1	—
45	6·7	0·0042
105	5·3	0·0040
165	4·3	0·0039
255	2·85	0·0041
350	1·85	0·0042
435	1·4	0·0040

The results show clearly the great retarding effect of hydrobromic acid on the rate of reaction, the gradual fall in the magnitude of the velocity coefficients in the solutions initially free from hydrobromic acid being due to the accumulation of this acid in the system as the action proceeds. In order to find the relative parts played by the non-ionised acid and the anion in the reaction, the simplest and most accurate method is to determine the relative concentrations of the $CHPhBr{\cdot}CO_2'$ ion in the solution of the sodium salt and in the acid solution in the presence of excess of hydrobromic acid, and to compare this ratio with the relative rates of displacement of bromine in the two solutions in question under equivalent conditions. The concentration of the $CHPhBr{\cdot}CO_2'$ ion in excess of hydrobromic acid is readily obtained by substituting in the equation for the influence of a common ion on the dissociation of a weak acid $[(a'c)c_0]/(1-a')c=K$, where c is the

concentration and K the dissociation constant of the weak acid, and c_0 the concentration of the common ion—in this case the $H^{\cdot}$ ion. As $N/5$-hydrobromic acid is ionised to the extent of about 90 per cent., and as c is 0·025 and K is 0·0035, we find for α', the new degree of dissociation, 0·019, and for $\alpha' c$, the concentration of the $CHPhBr{\cdot}CO_2'$ ion, 0·000475. Assuming that sodium phenylbromoacetate is ionised to the extent of 86 per cent. in $N/40$-solution, which must be very near the true value, the concentration of the anion in this solution is 0·0215, and the ratio of the concentrations of the $CHPhBr{\cdot}CO_2'$ ion in the two solutions is therefore 0·0215 : 0·000475, or about 45 : 1. It will be shown in the next section that the velocity coefficient for the hydroxylation of the sodium salt at 25° is about 0·0156, whereas the corresponding coefficient for the free acid in $N/5$-hydrobromic acid is 0·00049, the ratio being 32 : 1. If in the latter solution only the anion was undergoing change, the velocity coefficient would be $0{\cdot}0156/45 = 0{\cdot}00035$. As the coefficient actually obtained is 0·00049, the conclusion must be drawn that the non-ionised acid is also reacting with water, although, allowing for the greater concentration, much more slowly than the corresponding ion. A simple calculation shows that under equivalent conditions the $CHPhBr{\cdot}CO_2'$ ion reacts with water about 120 times as fast as the non-ionised acid.

In view of this interesting result, the data for phenylchloroacetic acid have been recalculated, using the slightly lower value of the dissociation constant given in the present paper. It has been found that if the $CHPhCl{\cdot}CO_2'$ ion is alone acted on by water the velocity coefficient would be 0·00044, whereas the observed value is 0·00048. The difference is scarcely beyond the limit of experimental error, so that the conclusion stated in the previous paper is fully confirmed.

The relative activities of the non-ionised halogen-substituted acids and the corresponding negative ions towards water are remarkable. Thus in the case of chloroacetic acid the activity of the ion is negligible in comparison with that of the non-ionised acid (T., 1907, **91**, 460). For phenylchloroacetic acid the ion alone is active, whereas for bromopropionic acid and phenylbromoacetic acid the relative activities of ion and acid are comparable. Results of this character are undoubtedly of great importance in elucidating the effect of the electric charge on the chemical behaviour of the ion. Their bearing will be discussed when fuller data are available.

From the results of the experiments in the presence of hydrobromic acid at 25° and 40·4°, described in table III, it can readily

be calculated that the temperature coefficient for 10° has the high value 4·0.

Hydroxylation of Sodium Phenylbromoacetate.

The hydroxylation of sodium phenylbromoacetate in aqueous solution is represented quantitatively by the equation

$$C_6H_5\cdot CHBr\cdot CO_2Na + H_2O \longrightarrow C_6H_5\cdot CH(OH)\cdot CO_2H + NaBr.$$

The results of typical experiments at 25° and 40·4° are given in table IV.

TABLE IV.

Sodium Phenylbromoacetate, N/40.

Temperature, 25·0°.			Temperature, 40·4°.		
t (min.).	*a* − *x*.	*k*.	*t* (min.).	*a* − *x*.	*k*.
0	4·2	—	0	3·15	—
10	3·6	0·0154	10	1·10	0·105
20	3·1	0·0152	15	0·55	0·116
40	2·3	0·0151	40	0·40	0·105
60	1·8	0·0141	—	—	—
80	1·4	0·0137	—	—	—

The approximate constancy of the coefficients *k* in the third column, calculated by the formula for a unimolecular reaction, shows that the formula in question is applicable. The slight diminution in the magnitude of the coefficients as the reaction proceeds is doubtless to be explained by the gradual accumulation of hydrobromic and mandelic acids in the system, resulting in the conversion of part of the remaining sodium salt into the free acid, which, as shown above, reacts less rapidly than the salt.

The temperature coefficient for 10°, calculated from the experiments at 25·0° and 40·4°, is 3·65, appreciably lower than the coefficient for the free acid. This is additional confirmation of the above conclusion that the reactions with the sodium salt and with the free acid in the presence of hydrobromic acid are not identical. In the case of phenylchloroacetic acid (*loc. cit.*), where the kinetic measurements indicated that the reaction was the same for the sodium salt and the free acid, the temperature coefficients of the two reactions are identical.

Hydroxylation of Sodium Phenylbromoacetate in the Presence of Excess of Sodium Hydroxide.

Measurements were made at 25° with *N*/40-sodium phenylbromoacetate and varying concentrations of sodium hydroxide.

The results of two typical experiments are quoted in table V. The values of k are calculated by the equation for a unimolecular reaction.

TABLE V.

Sodium Phenylbromoacetate, N/40.

Sodium hydroxide, $N/40$.			Sodium hydroxide, $0{\cdot}312N$.		
t (min.).	$a-x$.	k.	t (min.).	$a-x$.	k.
0	7·9	—	0	7·6	—
15	6·05	0·0178	10	6·45	0·0164
25	4·95	0·0187	25	4·8	0·0184
35	4·15	0·0184	40	3·75	0·0177
55	3·0	0·0176	65	2·4	0·0177

The results show that the reaction is slightly faster when $N/40$-sodium hydroxide is present along with the sodium salt, doubtless owing to the fact that the solution in those circumstances remains alkaline throughout. A further increase in the sodium hydroxide concentration has no accelerating effect, but, if anything, a slight retarding action. It follows that the action of hydroxyl ions on sodium phenylbromoacetate is quite negligible in comparison with that of water, as already found for sodium phenylchloroacetate.

It may be pointed out that bromine is displaced from phenylbromoacetic acid and its salts about ten times as fast as chlorine is displaced from phenylchloroacetic acid and its compounds under equivalent conditions. Approximately the same ratio has previously been obtained in the investigation of other halogen-substituted acids (Senter, *Zeitsch. physikal. Chem.*, 1910, **70**, 511; P., 1908, **24**, 89).

In conclusion, we desire to thank the Government Grant Committee of the Royal Society for a grant part of which has been used to defray the expenses of this investigation.

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[*Received, June 14th*, 1916.]

LVII.—*Interaction of Iodine and Thioacetamide in Aqueous and Alcoholic Solutions.*

By Prafulla Chandra Rây and Manik Lal Dey.

Evidence has from time to time been adduced in support of the view that in the presence of mercuric nitrate, as also of mercuric, cupric, and platinic chlorides, tautomeric change in certain organic thio-compounds is brought about; in other words, thiocarbamide, thioacetamide, etc., assume the labile form containing the thiol group (for example, $CH_3 \cdot CS \cdot NH_2 \longrightarrow CH_3 \cdot C(SH) : NH$), and the primary reaction is of the type

$$-SH + Hg(NO_2)_2 = -S \cdot HgNO_2 + HNO_2,$$

nitrous acid and a mercury mercaptide nitrite being thus formed (P., 1914, **30**, 140, etc.). It has also been shown that tautomeric changes of similar character can equally be effected through the agency of monochloroacetic acid in the case of thiocarbamide (T., 1914, **105**, 2159).

Free halogen in the shape of iodine has also been successfully employed by Werner in effecting the tautomerisation of thiocarbamide, the product of the interaction being formamidine disulphide (T., 1912, **101**, 2166).

The possibility suggested itself that thioacetamide under the action of iodine might undergo similar transformation. This expectation has been realised, but the reaction has not been so simple as in the preceding instance. This is easily accounted for when it is borne in mind that thioacetamide is more complex in structure than the carbamide.

The first stage of the reaction would seem to conform to the generic type:

$$CH_3 \cdot CS \cdot NH_2 \longrightarrow CH_3 \cdot C(:NH) \cdot SH + I \longrightarrow CH_3 \cdot C(:NH) \cdot S\cdot + HI.$$

The sulphur, however, becomes detached from the residue, and there is formed the complex $CH_3 \cdot C(:NH)\cdot$, which in turn acts on two molecules of water, thus:

$$CH_3 \cdot C(:NH)\cdot + 2H_2O + I = CH_3 \cdot CO_2H + NH_3 + HI.$$

The nascent hydrogen readily combines with iodine, giving rise to a second molecule of hydrogen iodide. The complete reaction may, therefore, be expressed as follows:

$$CH_3 \cdot C(:NH) \cdot SH + I_2 + 2H_2O = CH_3 \cdot CO_2H + NH_4I + HI + S.$$

The ultimate products of the reaction are thus found to be acetic acid, ammonium iodide, hydrogen iodide, and free sulphur.

If, however, an alcoholic solution of thioacetamide is substituted, the reaction proceeds in somewhat the above direction, only, in place of acetic acid, the corresponding ester is obtained, and instead of a second molecule of hydrogen iodide, a molecule of ethyl iodide is formed. The first stage of the reaction is the same as above, but in the second stage it evidently takes a new direction, thus:

$$CH_3{\cdot}C(:NH){\cdot} + 2EtOH + I = CH_3{\cdot}CO_2Et + NH_3 + EtI.$$

The complete reaction may, therefore, be expressed as follows:

$$CH_3{\cdot}C(:NH){\cdot}SH + 2EtOH + I_2 \longrightarrow CH_3{\cdot}CO_2Et + EtI + NH_4I + S.$$

As water and alcohol are of the same type, it was reasonable to anticipate that with alcohol the reaction would be according to the following equation:

$$CH_3{\cdot}C(:NH){\cdot} + O\,|\,EtH + EtO\,|\,H + I = CH_3{\cdot}CO_2Et + NH_2Et + HI,$$

that is, instead of ammonia, substituted ammonia or ethylamine would be formed; the product was, however, ammonia, or, rather, ammonium iodide, and, moreover, no free hydrogen iodide was detected, as in the previous case, the reacting liquid being neutral. The reaction may also be explained on the theory of hydrolysis, in which case a mere trace of an acid (in this case hydriodic acid) would be sufficient to start the reaction, for it will be seen that more acid will be formed during the progress of the reaction, thus:

$$CH_3{\cdot}C(:NH){\cdot}SH + 2H_2O = CH_3{\cdot}CO_2H + NH_3 + H_2S.$$
$$H_2S + I_2 = 2HI + S.$$

Thus there are two molecules of hydrogen iodide for every molecule of ammonia, or, in other words, free hydrogen iodide is formed, together with ammonium iodide.

Although this simple alternative explanation seems plausible in the case of an aqueous solution of thioacetamide, it does not hold good in the case of an alcoholic solution. For one would expect ethylamine to be produced, thus:

$$CH_3{\cdot}C(:NH){\cdot}SH + 2EtOH = CH_3{\cdot}CO_2Et + EtNH_2 + H_2S,$$

whilst ammonia is actually found. The main interest of the present investigation evidently centres round the fact that in the condensation of thioacetamide with, say, chloroacetaldehyde, a tautomeric change of the former is involved and a thiazole is formed, thus:

$$\begin{matrix} H{\cdot}C{:}O \\ H_2CCl \end{matrix} + \begin{matrix} HN \\ HS \end{matrix}\!\!>\!C{\cdot}CH_3 \longrightarrow \begin{matrix} HC{\cdot}N \\ HC{-}S \end{matrix}\!\!>\!C{\cdot}CH_3.$$

In the present instance the sulphur and nitrogen, instead of

contributing towards the formation of a ring compound, become detached from the parent substance.

Experimental.

Thioacetamide and Iodine in Aqueous Solution.

To a solution of thioacetamide in water iodine is added in small quantities at a time, and the flask vigorously agitated and heated on the water-bath. During the initial stages of the reaction the iodine is absorbed very slowly. The formation of hydrogen iodide, however, favours the dissolution of the iodine, and the decolorisation of the solution becomes more rapid; sulphur continually separates out and coagulates. The operation is stopped when no more iodine is absorbed. The sulphur is now filtered off, and the filtrate distilled. The residue is found to be ammonium iodide with a slight excess of iodine, which is removed by heating on the water-bath. The ammonium iodide was recrystallised, and analysis showed it to be pure. The distillate consists of free acetic and hydriodic acids.

Thioacetamide and Iodine in Alcoholic Solution.

In this case, owing to the solubility of iodine in alcohol, the reaction, which is carried out in the cold, proceeds more rapidly. It was noticed, however, that when the solution, coloured deep red by excess of iodine, was allowed to remain over night it was not only completely decolorised, but was capable of absorbing a further quantity of iodine. The operation requires at least forty-eight hours for completion. The sulphur is filtered off, and the filtrate subjected to distillation. That the residue was ammonium, and not ethylammonium iodide, was proved by converting it into the chloride and the latter into the corresponding platinic salt. (Found, Pt=43·69. Calc., Pt=43·66 per cent.)

The distillate consisted of an alcoholic solution of ethyl acetate and ethyl iodide with distinct traces of hydrogen sulphide, which was removed by shaking with precipitated mercuric oxide. The presence of the former was proved in the following manner. The alcoholic filtrate had a neutral reaction, and gave a precipitate of silver iodide with an acetone solution of silver nitrate. This showed the existence of ethyl iodide. Ethyl acetate was detected by its fruity odour, as also by the characteristic tests for acetic acid after hydrolysis with sodium hydroxide.

Summary and Conclusion.

Thioacetamide and iodine interact in aqueous solution to form acetic acid, hydrogen iodide, ammonium iodide, and free sulphur.

In alcoholic solution the products are ethyl acetate, ethyl iodide, ammonium iodide, and free sulphur.

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[*Received, April 1st,* 1916.]

LVIII.—*Conversion of Aliphatic Nitrites into Nitro-compounds.*

By PAÑCHĀNAN NEOGI and TĀRINICHARAN CHOWDHURI.

ONE of us has already shown (Neogi, T., 1914, **105**, 2371) that the idea of tautomerism cannot properly be applied to the case of nitrites and nitro-compounds, and has advanced the theory that the formation of aliphatic nitrites and nitro-compounds may be attributed to two causes, namely, (1) isomeric conversion of nitrites into nitro-compounds, and (2) formation of unstable intermediate additive compounds. The present investigation was undertaken with the object of finding experimental evidence of the conversion of aliphatic nitrites into nitro-compounds. Experiments show that aliphatic nitrites are partly converted into the corresponding nitro-compounds by the action of heat.

Conversion of Ethyl Nitrite into Nitroethane.

The apparatus employed in the case of methyl and ethyl nitrites was the same. The solution of the nitrite in paraffin oil was placed in a flask provided with an upright spiral condenser, which in turn was connected with a combustion tube about 90 cm. long, filled with asbestos-wool (in order to expose a large surface to the gaseous nitrites), and heated in an asbestos box provided with a thermometer. The gaseous nitrite was carried into the tube by means of a slow stream of dry carbon dioxide. The nitro-compound was collected in a U-tube immersed in cold water, and the escaping nitrite in absolute alcohol or methyl alcohol cooled in ice-water.

Fifteen or 20 c.c. of the nitrite solution were used at a time. A 25 per cent. solution is convenient, and a 50 per cent. solution loses nitrite very rapidly. As the gaseous nitrite remains only

momentarily in contact with the heated asbestos, the yield of the nitro-compound is small, the greater portion of the nitrite escaping conversion. Within four or five hours the greater part of the dissolved nitrite passes through the heated tube. The oily nitro-compound was easily recognised by the formation of the sodium compound on the addition of alcoholic sodium hydroxide solution.* The nitro-compound was also reduced to the corresponding amine, which was converted into the platinichloride. (Found, Pt = 38·79. Calc., Pt = 39·00 per cent.)

The conversion commenced at 100°, and was fairly rapid at 120—130°, when oily drops began to collect in the empty U-tube. At the end of four to five hours about 1 c.c. of the liquid collected, which responded very readily to the alcoholic sodium hydroxide test. If the temperature is raised to about 135—150°, acetaldehyde and acetic acid are produced along with the nitro-compound. At 150—180° the acid is the main product of the decomposition. The formation of the aldehyde and the acid is readily explained by the fact that at a higher temperature the nitrite dissociates into alcohol and nitrous acid, the latter decomposing into nitric acid, and the higher oxides of nitrogen which oxidise the alcohol to the aldehyde and the acid. The best yield of the nitro-compound is obtained at 120—130°.

In order to ascertain if a better yield is obtained when an alcoholic solution of the nitrite is heated in a sealed tube, 10 c.c. of the solution were sealed in a glass tube and heated in a furnace. During the act of sealing, the part of the tube containing the solution should be immersed in a freezing mixture, as otherwise explosions take place. The yield, however, was not very satisfactory. When heated at 100° for five to six hours the solution, after distilling off the unchanged nitrite and alcohol, gave about 1 c.c. of liquid, which responded to the test for a nitro-paraffin and boiled at 98—104°. Owing to the admixture of alcohol, the actual boiling point was lowered. If, however, the solution was heated to 150° for twelve to fifteen hours, the tube was found to contain acetic acid, formed by the oxidation of the alcohol by nitric acid and higher oxides of nitrogen produced from the decomposition of the nitrite, besides free nitrite. The proportion of the nitro-compound was very small.†

* Blank experiments were made with nitrites, nitrates, alcohols, aldehydes, and acids containing methyl, ethyl, propyl, *iso*propyl, butyl, and amyl groups which were found not to give the alcoholic sodium hydroxide test.

† In the experiments with the different nitrites the liquid obtained in five or six experiments was collected and fractionated, and the alcohol, aldehyde, acid, and nitro-compounds were identified.

Conversion of Methyl Nitrite into Nitromethane.

The gaseous methyl nitrite was absorbed in well-cooled paraffin oil, and the solution obtained in this way was also cooled, during experiment, in ice, while a slow current of carbon dioxide was passed through it. Methyl nitrite being more volatile than the ethyl compound, a 20 per cent. solution was found convenient to use. The general behaviour of methyl nitrite is similar to that of ethyl nitrite. The conversion commenced at 100°, and at 120—130° oily drops of nitromethane collected. At a higher temperature formaldehyde and formic acid were obtained along with the nitro-compound, just as the corresponding aldehyde and acid were produced in the case of ethyl nitrite. Attempts were made to heat the nitrite dissolved in methyl alcohol in a sealed tube, but owing to the extreme volatility and inflammability of the methyl nitrite, the tube could not be sealed, even when cooled in a freezing mixture, as constant explosions took place.

Conversion of iso*Propyl Nitrite into β-Nitropropane.*

A 25 per cent. solution of *iso*propyl nitrite in paraffin oil was employed, the spiral condenser, inserted into the mouth of the flask, being two-thirds filled with water. The receiving U-tube was kept in water at 25—30°. At 100°, after four to five hours, a few minute drops of nitro-compound were obtained. At 125° the yield was greater, the best result being obtained at 125—130°. At higher temperatures the corresponding aldehyde and acid were produced, in addition to the nitro-compound. The quantity of available *iso*propyl alcohol being small, the platinichloride of the amine was not prepared.

Conversion of n*-Propyl Nitrite into Nitropropane.*

There was no necessity for using solutions of *n*-propyl nitrite in paraffin oil, as its boiling point is comparatively high, namely, 58—60°. On passing its vapour as usual through the tube, drops of nitro-compound collected at 125—130°. At a higher temperature the corresponding aldehyde was formed, and above 150° the acid was almost the main product.

The nitrite was also heated in a sealed tube in a furnace for five to six hours at 120°. After opening the tube, the liquid on fractionation yielded a fraction boiling at 126—128°, which, on reduction, furnished the corresponding amine. (Found, Pt=36·61. Calc., Pt=36·93 per cent.)

Conversion of iso*Butyl Nitrite into Nitro*iso*butane.*

*iso*Butyl nitrite, which boils at 70°, was passed through the heated tube, and also heated in a sealed tube. In the first case at 120—125° an oily liquid collected in the U-tube, which, in addition to the nitro-compound, contained butyl alcohol, butaldehyde, and butyric acid. At a higher temperature, the percentage of butyric acid becomes greater. The products from four experiments were mixed and fractionated. The fraction boiling at 130—135° was reduced to the corresponding amine and the platinichloride prepared. (Found, Pt=34·87. Calc., Pt=35·07 per cent.)

On heating the nitrite in a sealed tube at 125°, small quantities of the nitro-compound were obtained along with butyl alcohol and butyric acid, the alcohol forming the major portion.

Conversion of iso*Amyl Nitrite into* iso*Nitropentane.*

When amyl nitrite was heated under a reflux condenser to 120°, nitrous fumes slowly appeared, and at 150° they were evolved in larger quantities. When heated at 150—180° for six to eight hours, the liquid, on distillation, was found to contain very little nitrite, the greater part being amyl alcohol. The last fraction, however, responded to the test for nitro-paraffins.

On passing the vapour of *iso*amyl nitrite through the heated tube at 120° a liquid collected in the receiving tube, which responded to the test for nitro-paraffins. The liquid, however, contained alcohol and acid as well, the former preponderating. The fraction boiling at 138—147°, obtained by fractionation of the products of four experiments, was reduced to the corresponding amine, the platinichloride of which was analysed. (Found, Pt= 38·94. Calc., Pt=39·23 per cent.)

It appears from the foregoing experiments that the production of aliphatic nitro-compounds is partly explained by the isomeric conversion of nitrites. In the preparation of nitro-compounds, either by the interaction of silver or mercurous nitrite and alkyl iodides or of alkyl sulphates and alkali nitrites, the substances are digested for many hours, and during the process of heating, even at 100°, partial conversion of nitrites into nitro-compounds would be possible, although in the case of gaseous nitrites like methyl and ethyl nitrites the formation of large quantities of nitromethane and nitroethane cannot possibly be due to isomeric conversion to a large extent. In the case of the preparation of the nitro-compounds, however, by heating mixtures of alkyl alkali sulphates and alkali nitrites, the alcohol formed by the decomposition of the alkyl sulphates or the aliphatic nitrites would dissolve large quantities

of the aliphatic nitrites, which on prolonged digestion would be partly converted into the corresponding nitro-compounds.

Influence of Moisture on the Conversion.

In order to study the influence of moisture, the gaseous nitrite was dried by passage through one or two calcium chloride tubes and then passed into the heated tube, when it was found that very little liquid collected in the receiving U-tube and most of the nitrite was passing out unchanged. This phenomenon was observed in the case of all the nitrites. It appears that the presence of moisture, which is always present in the rapidly dried nitrites, facilitates the conversion of the nitrite into the nitro-compound.

In order to ascertain if the presence of larger quantities of moisture in the gaseous nitrites gives rise to a larger percentage of nitro-compounds, the nitrites were passed through a wash-bottle containing water before entering the heated tube. It was found that when surcharged with moisture the nitrite dissociated more rapidly, yielding larger quantities of alcohols, aldehydes, and acids without any appreciable increase in the yield of the nitro-compound. It appears that in the presence of traces of moisture, two reactions proceed simultaneously, namely, the conversion of the nitrite into nitro-compound and the dissociation of the nitrite; and with the increase in the proportion of water the latter reaction proceeds with greater rapidity.

Reduction of Aliphatic Nitrites to Amines.

Gaudion (*Ann. Chim. Phys.*, 1912, [viii], **25**, 125) observed that by passing a mixture of hydrogen and aliphatic nitrites over heated finely-divided nickel or copper, amines are obtained, but he was unable to explain definitely how amines could be produced by the reduction of nitrites. We have also obtained amines by passing a mixture of the nitrites and hydrogen through a heated tube containing reduced nickel.

The formation of small quantities of amines by the reduction of aliphatic nitrites can now readily be explained in view of the above experiments. It is the nitro-compounds that are actually formed which undergo reduction to amines, and not the nitrites themselves. Sabatier and Senderens (*Compt. rend.*, 1902, **135**, 225) have, as a matter of fact, shown that aliphatic nitro-compounds are thus reduced to amines by hydrogen in presence of heated nickel.

Theories of the Formation of Aliphatic Nitro-compounds.

The partial conversion of aliphatic nitrites into nitro-compounds has a theoretical bearing on the formation of nitro-compounds.

Neogi (T., 1914, **105**, 2371) has already shown that the theory of tautomerism cannot be applied to the aliphatic nitrites and nitro-compounds, as heavy atoms of silver and mercury as well as heavy alkyl radicles cannot be supposed to oscillate between an oxygen and a nitrogen atom, the true tautomerides being nitro-compounds and nitrolic acids. He therefore advanced two other hypotheses to account for the formation of nitro-compounds, namely, (1) isomeric conversion, and (2) formation of unstable additive compounds. The results of the present investigation show that the conversion of aliphatic nitrites into nitro-compounds takes place at a higher temperature, but, as the yield is very small, it alone is incapable of explaining the formation of the large quantities of nitro-compounds obtained by the interaction of silver or mercurous nitrite and alkyl iodides. The interaction of silver or mercurous nitrite and alkyl iodides is completed at 100°, whilst the conversion of aliphatic nitrites into nitro-compounds, although commencing at 100°, does not proceed to an appreciable extent below 120—130°. Moreover, ethyl and methyl nitrites, being gaseous, escape at the moment of formation, and have little chance of conversion into the nitro-compounds during digestion. In the case of the higher nitrites, however, especially when the interaction of alkyl sulphates and alkali nitrites takes place at a higher temperature, isomeric conversion would be partly responsible for the formation of the nitro-compounds.

The theory of isomeric conversion not being adequate to explain the formation of the entire quantity of the nitro-compound actually produced, the formation of unstable intermediate compounds becomes the only alternative explanation of the formation of the aliphatic nitro-compounds. This additive hypothesis is summarised thus: Nitrous acid, which forms aliphatic nitrites, and not nitro-compounds, with alcohols, evidently possesses the oxylic constitution HO·NO, and the inorganic nitrites, including silver and mercurous nitrites, being obtained simply by the neutralisation of nitrous acid with inorganic oxides, would also possess the same constitution. When the alkyl iodides react with silver or mercurous nitrite, or when the alkyl sulphates react with alkali nitrites, two reactions take place, namely, (1) the aliphatic nitrites are obtained by direct interchange, and (2) unstable intermediate compounds are formed, which decompose with the formation of nitro-compounds, thus:

$$AgO\cdot N{:}O + C_2H_5I = AgO\cdot N(C_2H_5)\cdot OI = C_2H_5\cdot NO_2 + AgI.$$
$$KO\cdot N{:}O + C_2H_5KSO_4 = KO\cdot N(C_2H_5)\cdot OKSO_4 = C_2H_5\cdot NO_2 + K_2SO_4.$$

The relative proportions in which the nitro-compounds would be produced would depend on the extent to which the intermediate

compounds are formed. As the nitrites and nitro-compounds are formed in many cases in almost equal quantities, the two reactions proceed in those cases to an almost equal extent. To the reactions thus indicated is to be added the effect of the partial conversion of the nitrites into nitro-compounds where the digestion takes place at a higher temperature. In the case of nitrous acid the intermediate compounds not being formed, no nitro-compounds are obtained.

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LIX.—*The Constitution of Coal.*

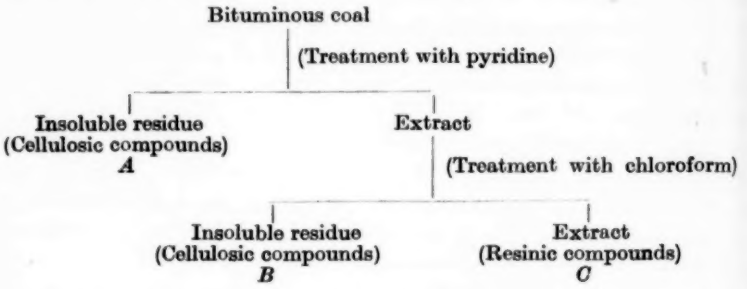
By DAVID TREVOR JONES and RICHARD VERNON WHEELER.

A DETAILED discussion of the various views held as to the probable origin of "coal," the material from which it is derived, and the manner of its formation is outside the scope of this paper. The general trend of opinion is that the material from which coal has been formed has been essentially vegetable. There is no consensus of opinion as to the manner of formation of coal, probably because attempts have been made to assign a common rationale to all the varieties, whereas there seems to be no adequate reason why different varieties, or, indeed, different accumulations of similar varieties, should not have been produced in different manners. The agencies that have produced coal from the original (vegetable) substances are generally supposed to be, in the first instance, decay through the agency of bacteria, followed by pressure, heat, and time.

The present research is an attempt to determine the chemical character of the main components of "coal," which, accepting the usual view as to its vegetable origin, we regard as essentially a conglomerate of cellulosic and resinic compounds.

It has been shown (T., 1913, **103**, 1706) that these two main constituents of bituminous coals (with which our experiments have mainly dealt) can be separated by means of solvents. Extraction of the dried coal with pure, dry pyridine brings about a partial separation, there being an insoluble residue consisting mainly of the cellulosic constituents. Further extraction of the soluble portion after it has been freed from pyridine, using chloroform or benzene, effects a further resolution, there being a soluble portion containing the resinic compounds and an insoluble residue

consisting of cellulosic compounds resembling in every respect those separated directly from the coal by means of pyridine. The scheme of separation is as follows:



That the residue *B*, insoluble in chloroform, is to be regarded as composed of cellulosic compounds in the coal conglomerate that possess (or acquire during extraction) the property of solubility in pyridine, rather than as resinic compounds that have lost the property of solubility in chloroform, is apparent from the following facts:

(1) *A* and *B* are infusible; *C* softens at about 100°.

(2) *C* on exposure to air undergoes some form of oxidation, exhibited also by resins, which exerts photochemical action on a sensitised plate. *A* and *B* under similar conditions have no such action (*loc. cit.*, p. 1713).

(3) On distillation in a vacuum at a given temperature *A* and *B* yield gaseous mixtures which closely resemble one another both in quantity and composition, and differ markedly in both respects from the gaseous mixtures obtained by distilling *C* under like conditions (*loc. cit.*, p. 1710).

(4) The liquid distillates from *A* closely resemble those from *B* both in quantity and kind, and bear no resemblance to those obtained from *C*. The liquid distillates from *A* and *B* represent but a small percentage of their weights, and in both cases consist almost entirely of phenols. *C* loses half its weight at 450° as liquid distillates, which contain all the components of tar obtained by the low-temperature carbonisation of coal, with the exception of phenols which are absent.

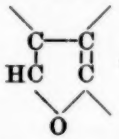
The Character and Composition of the Cellulosic Compounds.

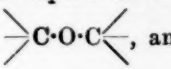
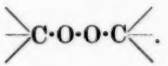
Boudouard's work (*Compt. rend.*, 1909, **148**, 348) has shown that unchanged celluloses, if present at all in bituminous coals, can only be present in minute quantities. The cellulosic compounds are degradation products of the original plant celluloses,

the extent to which change has taken place being indicated by comparison of the ultimate analysis of cellulose with that of either portion *A* or portion *B* of a bituminous coal.

The most striking point of resemblance between the "cellulosic compounds," *A* or *B*, separated from coal, and cellulose is that both yield phenol or phenols on destructive distillation. Wichelhaus (*Ber.*, 1910, **43**, 2922) found that cellulose yielded phenol, but homologues of phenol were not obtained. In the case of the cellulosic compounds in coal, analyses of the phenols obtained on distillation show a composition ranging between that of the cresols and the xylenols.

The production of phenols on destructive distillation is occasioned by the presence of the furan grouping,



in the substance distilled. This grouping is stable, and it can readily be understood that it should survive the degradation changes to which the cellulose molecule has been subjected. These changes would, most naturally, be such as would bring about the elimination of hydroxyl groups and hydrogen, with the consequent formation of oxide or ether groupings of the structure  , and possibly of peroxide groupings,  . The furan grouping would remain unchanged.

There is thus reason to believe that the compounds that constitute the cellulosic constituents of coal may not comprise many types. This suggestion is borne out by the fact that *A* and *B* classes of cellulosic compounds yield on distillation below 450° gaseous and liquid products almost identical in composition. The readily decomposable portions of the cellulosic compounds *A* and *B* thus closely resemble one another in constitution, and the same may be true of the more stable portions.

The question arises whether in some of the cellulosic derivatives the characteristics of the cellulose grouping may not have disappeared entirely and molecules approximating in structure to that of carbon have resulted.

The Presence of "Free" Carbon in Coal.

The idea seems to be widespread that most coals contain a certain proportion of free carbon, and the difference between one

class of coal and another, between bituminous and anthracitic coals, for example, has been ascribed to a difference in the proportion of free carbon present. This view appears to be maintained largely on account of the colour and general appearance *en masse* of coal, which become more carbon-like the older the coal measure, and from the knowledge that the parent substance of coal has been subjected to various degrees of molecular attrition, involving the loss of hydrogen and oxygen, which, it is supposed, may have been sufficient in the case of some components to have effected complete carbonisation.

The argument respecting the colour of coal may be answered by pointing out that the portions of coal insoluble in pyridine and chloroform are indistinguishable in appearance from Cross and Bevan's dehydrated cellulose ("pseudo-carbon"), a carbon-like substance which contains no free carbon (*Phil. Mag.*, 1882, [v], **13**, 325).

The agencies that have in the course of time produced coal, presumably from vegetable matter, are bacterial decay, heat, and pressure. Excluding as highly improbable the possibility of micro-organisms having effected a segregation of free carbon, there remain for consideration the influence of heat and pressure.

It is doubtful whether any coal-seam has, in the normal course of events, attained a temperature as high as 300°. Below this temperature every variety of distillate ordinarily found in coal-tar begins to make its appearance, and these compounds in an uncombined state are not normally present in coal. There are isolated instances of the occurrence of paraffin waxes oozing from coal-seams, usually in the neighbourhood of a fault (for example, Cohen and Finn, *J. Soc. Chem. Ind.*, 1912, **31**, 12), which are accounted for by local heating, due probably to earth movement, at some period in the history of the seam, just as there are instances of complete carbonisation (coking) of part of a coal-seam by volcanic intrusion. It seems impossible, however, that coals in general can ever have approached during their formation a temperature of 300°, and such a temperature is too low to effect complete carbonisation.

The effect of pressure is adverse to molecular disintegration, as the polymerisation of hydrocarbons under pressure instances. It is noteworthy that hydrogen is found in but small quantity when it results from decompositions carried out under high pressures. For example, Ipatiev (*Ber.*, 1911, **44**, 2978), in the course of experiments in thermal decomposition, observed that with increasing pressure the gases became richer in paraffins and poorer in carbon monoxide and hydrogen.

There seems, in fact, no reason to believe that any of the factors, singly or combined, involved in the formation of coal can have brought about the complete carbonisation of any portion of the mother substance of coal. On the other hand, the existence in coal of substances the molecules of which are similar in type to the carbon molecule must be presumed. Dimroth and Kerkovius (*Annalen*, 1913, **399**, 120) have shown that the carbon molecule contains the fluorene grouping, whilst Pictet and Ramseyer (*Ber.*, 1911, **44**, 2486) have extracted hexahydrofluorene from Montrambert coal. Moreover, both carbon and coal yield benzenehexacarboxylic acid (mellitic acid) on oxidation, showing that in both cases there are molecules present the structure of which involves a six-carbon ring, each carbon atom being attached to another carbon atom.

The Resinic Compounds.

The "resinic" compounds in coal are more diversified than the "cellulosic," and are presumably derived from the numerous substances, such as gums, resins, starches, sugars, etc., in the original plants. They comprise compounds containing residual alkyl, naphthene, and unsaturated hydroaromatic groupings linked to larger and more complex groupings, the latter being the polymerisation and degradation products of the gums, resins, etc., and, it may be, to some extent of the celluloses. It is probable that the original unsaturated hydrocarbons present have, under the influence of pressure, either become polymerised or concerted into compounds containing the naphthene grouping.

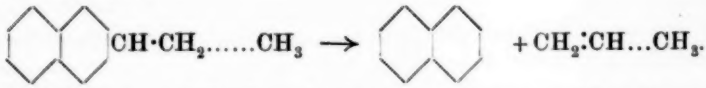
It has been shown in previous papers that all the compounds obtained as low-temperature distillates from coal (with the exception of small quantities of paraffins) are decomposition products and are not present in a free state in the coal. In order to account for their appearance in coal distillates at low temperatures, under conditions which preclude the possibility of their pyrogenic synthesis, we have advanced an hypothesis of "bound" molecules (T., 1914, **105**, 141) which satisfactorily accounts for the production of olefines, paraffins, and naphthenes. The distillation of aromatic compounds at temperatures below 350° requires further explanation. The aromatic compounds distilled from bituminous coals at a temperature of 300—350° form picrates the characteristic stability of which in water shows them to be homologues of naphthalene, and give analyses corresponding with that of dimethylnaphthalene.*

* Acenaphthene, the picrate of which is also stable in water, has a much higher boiling point than the aromatic compounds distilled from coal.

Brooks and Humphrey (*J. Amer. Chem. Soc.*, 1916, **38**, 393), as a result of experiments on the thermal decomposition at temperatures below 420° of a synthetic mixture having the average composition of tetracosylbenzene, $C_6H_5 \cdot C_{24}H_{49}$, from which they obtained benzene and toluene, have suggested the possibility of such a change as the following:

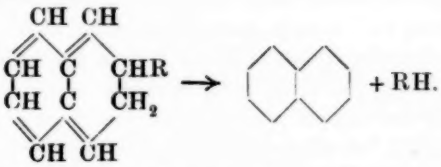
$$R \cdot C_nH_{2n+1} \longrightarrow R \cdot H + C_nH_{2n} \text{ (Olefine).}$$

For example:



Naphthalene and its homologues are, however, neither frequent nor plentiful constituents of plant life, and cannot be the direct source of more than traces in coal of compounds containing aromatic (as distinct from hydroaromatic) and naphthalene groupings in either the free or the "bound" condition; and it is unlikely that during the formation of coal, under the influence of pressure, hydrogen should be eliminated from such hydroaromatic compounds as may originally have been present. Nor can the aromatic compounds found in coal distillates be formed from "bound" hydroaromatic compounds by elimination of hydrogen during distillation, for they appear at a lower temperature than that at which hydrogen is eliminated from dihydronaphthalene (T., 1915, **107**, 1582).

The mechanism of decomposition of santanous acid, $C_{15}H_{10}O_3$, between 300° and 350°, which does not involve the elimination of hydrogen, suggests that the mode of formation of naphthalene derivatives from hydrogenated nuclei in coal may be according to the following scheme:



As regards the nature of the oxygenated compounds present in the resinic constituents of coal, the chemical indifference of the bulk of the coal towards saponifying and hydrolysing reagents generally makes it difficult to believe that much of the oxygen can be present in any reactive group, such as the hydroxylic or carboxylic. It is possible that the chemical indifference of coal is due to the oxygen being present in the groupings C·O·C·O·C, C·O·C, and C·O·O·C as a constituent of cyclic and, to a less extent, of open-chain oxides. Such a condition would account

also for the occurrence of water in the distillates from dried coal (often considered as necessarily implying the presence of hydroxyl groups), for Senderens (*Compt. rend.*, 1908, **146**, 1311) has shown that ethyl ether, for example, $CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_3$, decomposes readily in contact with dehydrated alumina, the mechanism of decomposition involving the elimination of water and the formation of ethylene. It should be noted, however, that Benedict and Bamberger (*Monatsh.*, 1890, **11**, 262) have shown that the methoxyl grouping, present in woods and lignites, is absent from bituminous coals (and cellulose).

Hydrocarbons in Coal.

The presence of traces of free hydrocarbons in different coals has been proved by Pictet and Ramseyer (*loc. cit.*), who isolated hexahydrofluorene, and by Pictet and Bouvier (*Ber.*, 1915, **48**, 930), who distilled a solid naphthene (melene, $C_{30}H_{60}$, m. p. 62—63°) from Pictet and Ramseyer's extract of a Montrambert coal. We have obtained solid paraffins corresponding with heptacosane, $C_{27}H_{56}$, from several British coals by extraction with pentane. The presence of complex unsaturated (olefinic) hydrocarbons is difficult of proof, but, since such hydrocarbons are important constituents of plants, can be assumed.

Apart from these traces of free hydrocarbons, the occurrence of which we have shown to be, in a sense, accidental, coal must contain hydrocarbons in a "bound" condition, which on distillation are set free in the manner already described. The "bound" paraffin hydrocarbons no doubt owe their origin to long-chain esters and acids, such as oleic, palmitic, and linolic acids, present in the original plants, although the manner of disappearance of the alcoholic and carboxylic groupings is, as in the parallel case of the formation of petroleum, largely a matter of conjecture.

The resemblance between low-temperature distillates from coal and certain varieties of petroleum is such as to have suggested a common origin, and Pictet and Bouvier (*loc. cit.*) have identified various naphthenes derived from coal with naphthenes derived from Galician and Canadian petroleums. We do not consider, however, that these similarities can be regarded as pointing to more than a partial identity of the parent substances of coal and petroleum, to the presence in both parent substances of compounds, such as aliphatic esters, which are common to both vegetable and animal remains.

The outstanding difference between the "petroleum" distilled from coal and the natural oils is the presence in the former of phenols. The difference is explicable when the conglomerate

character of coal is borne in mind and when it is remembered that phenols are distilled only from the cellulosic portions. The absence of phenols from petroleum suggests that its parent substance contained no material of cellulosic structure, for phenols are highly stable compounds and would withstand the temperature of the oil springs. The possibility of celluloses having been present originally and of their having undergone transformation with entire loss of structure must be admitted, but on the whole the absence of phenols from petroleums must be regarded as evidence in favour of their non-vegetable origin.

Summary.

Coal is considered to have been formed from decayed vegetable matter by the action of pressure and temperature. The temperature cannot have approached 300°.

The coal conglomerate can be resolved by means of solvents into cellulosic and resinic portions.

The cellulosic derivatives contain compounds the molecules of which possess the furan structure and yield phenols when destructively distilled. There are also compounds present the molecules of which have structures resembling that of the carbon molecule, but it is unlikely that "free" carbon is present in coal. The cellulosic derivatives are probably few in type.

The resinic derivatives contain compounds in which alkyl, naphthene, and unsaturated hydroaromatic radicles are attached to larger and more complex groupings. It is doubtful whether aromatic groupings are present. Under the influence of pressure the bulk of the resinic derivatives have become highly polymerised. The oxygenated resinic derivatives are chiefly oxides, probably cyclic oxides; esters, lactones, anhydrides, acids, and ketones are absent or present only in small quantity.

Hydrocarbons exist in the resinic portion of coal; saturated hydrocarbons (paraffins) are, however, present in small quantity only.

The main distinction between low-temperature distillates from coal and petroleum is the absence of phenols in the latter. This is held to be corroborative evidence of the non-cellulosic origin of petroleum.

ESKMEALS,
CUMBERLAND.

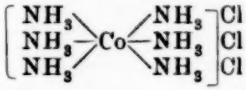
[*Received, June 9th*, 1916.]

CX.—*A Cyclic Theory of the Constitution of Metalammines and of Ferro- and Ferri-cyanides.*

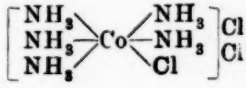
By John Albert Newton Friend.

In 1908 a cyclic theory was suggested to account for the constitution of complex inorganic salts (Friend, T., 1908, **93**, 1006, "Theory of Valency," first ed., 1909), and the object of the present paper is to develop this theory and to point out the interesting manner in which it accords with recent additions to our knowledge of the ferro- and ferri-cyanides.

The cyclic theory may be illustrated by reference to hexammine cobaltic chloride, $[Co(NH_3)_6]Cl_3$, and monochloropentammine cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, to which Werner ascribes the formulæ



and



respectively.

There are several fundamental objections to these schemes, namely:

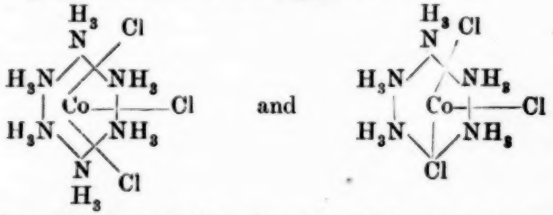
(1) The dissociable chlorine atoms hover in an indefinite manner round the nucleus as a whole, and are not attached to any particular point on or within it. The nucleus thus exerts merely a general attractive force akin to that of gravity, and isomerism due to a definite spatial arrangement of the chlorine atoms outside the nucleus is impossible. This indefiniteness is at once the strength and weakness of the theory: its strength, because it may be interpreted to accord with almost any theory or suggested grade of chemical combination; its weakness, because, whilst assuming a definite valency for cobalt, nitrogen, and hydrogen atoms, it denies an equally definite valency to chlorine, unless, as in the case of one atom in the pentammine salt, it happens to fall within the nucleus.

(2) Cobalt is credited with a valency of six. This, however, is opposed to the general behaviour of the element. Werner himself realised this when first promulgating his theory, and "overcame" the difficulty by assuming that three NH_3-groups were attached to the cobalt by principal valencies—that is, valencies ordinarily exerted by an element—whilst the remaining three NH_3-groups were attached by secondary, auxiliary, or residual valencies. Recent researches indicate that there is no real difference between the two kinds of valency, and Werner

himself is now apparently of the same opinion. (*Ber.*, 1913, **46**, 3674. See Dubsky, *J. pr. Chem.*, 1914, 11, **90**, 61.)

(3) The chlorine atoms outside the nucleus are regarded as dissociable because they are loosely attached to the nucleus. The other atoms within the nucleus cannot dissociate because they are attached direct to the cobalt atom. This is clearly an incorrect assumption. In potassium chloride we have a highly dissociable salt, yet the chlorine is attached directly to the metal, and there is no apparent reason why the same should not apply to, at any rate, the chlorine atom attached to the cobalt in the pentammine derivative. Dissociation is intimately connected with hydration (Walker, McIntosh, and Archibald, T., 1904, **85**, 1098; Bousfield and Lowry, *Phil. Trans.*, 1904, **204**, 282; *Trans. Faraday Soc.*, 1905, **1**, 197; 1907, **3**, 123), and is not rendered impossible simply because the atom in question is attached to a metal. The chlorine atom in the ring is tervalent and saturated; the dissociable chlorine atoms are only univalent or unsaturated, and are hence capable of hydration.

In view of the remarkable success which has attended the application of definite valency values to elements in the domain of organic chemistry, and without which the constitutions of such complex molecules as indigotin, etc., could never have been satisfactorily unravelled, it seems to the present author exceedingly unwise to reject the same definite valency values in attempting to explain the constitution of complex inorganic derivatives. There is no apparent reason why the one group of complexes should be governed by different laws from the other, and just as the most complex organic derivatives are closed-chain or ring compounds, so it is possible that inorganic complexes may have analogous cyclic constitutions. For the two cobaltammines under discussion the following cyclic formulæ are suggested:



respectively. These may, for the sake of brevity, be represented by the same schemes as are normally used by Werner, namely, $[Co(NH_3)_6]Cl_3$ and $[Co(NH_5)Cl]Cl_2$, the nucleus within the square bracket constituting the positive ion as before.

The main points of difference between the author's cyclic and Werner's theories are as follows:

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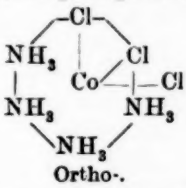
(1) The dissociable chlorine atoms are attached directly to the cobalt atom.

(2) The cobalt and chlorine atoms are credited with valency values that are strictly in accord with their known behaviour.

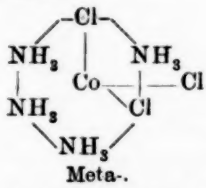
(3) In the pentammine salt the one chlorine atom is incapable of separate dissociation, not because it is attached to the cobalt, but because it forms part of the ring.

(4) The cobalt atom lies in the ring from which it cannot easily escape for purely physical reasons. In the hexammine derivative the cobalt is not attached by any valency bond to the ring, and on ionisation the cobalt atom remains surrounded by it, thus constituting the complex positive ion. This is an interesting view, because it probably throws light on the structure of hydrated ions. Thus, as the result of physico-chemical measurements, many metallic ions are known to be associated with water molecules which retard their mobility. The water is not combined with the atom in any chemical sense, but forms what Kohlrausch terms "an atmosphere" about it, the complex as a whole moving through the solution (Kohlrausch, *Proc. Roy. Soc.*, 1903, **71**, 338; *Sitzungsber. Preuss. Akad. Wiss.*, 1902, **26**, 579). These aqueous atmospheres probably take the form of rings or shells of water molecules surrounding the metallic atom, and joined together by the atoms of oxygen exerting their full quadrivalent power.

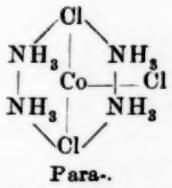
Dichlorotetrammine cobaltic chloride, $[Co(NH_3)_4Cl_2]Cl$, may be written, according to the cyclic theory, in three different ways, according as the chlorine atoms within the ring take up the ortho-, meta-, or para-positions. Thus:



Ortho-.



Meta-.



Para-.

It does not follow that the three isomerides corresponding with these formulæ will be stable or even capable of preparation, and in any case their chemical properties will be closely similar. Two isomerides have been isolated, but at present it is impossible to determine with which formulæ they correspond. It will be observed that, as in Werner's schemes, no isomerism is possible in the hexa-, penta-, or tetra-ammines by simply varying the positions of the dissociable chlorine atoms, since these are attached, not to the ring, but to the central cobalt atom.

The last member of the series, namely, trichlorotriammine cobalt, $[Co(NH_3)_3Cl_3]$, may likewise be represented in three

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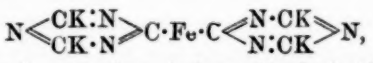
different ways, and none of the forms will ionise on solution, for all the chlorine atoms are within the ring.

In each of the foregoing examples the complex ions have been electropositive. Many electronegative complex ions are known, the most important of which probably are the cyanides containing iron.

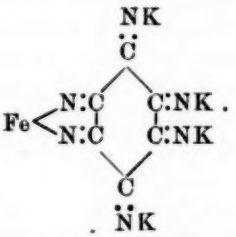
Potassium Ferrocyanide.

Many formulæ have been suggested to illustrate the constitution of potassium ferrocyanide. Both Graham ("Elements of Chemistry," 1842, **1**, 200) and Erlenmeyer ("Lehrbuch der organischen Chemie," 1867, 148) considered that the CN-groups were present in sets of three, as in cyanuric acid, so that the formula would be

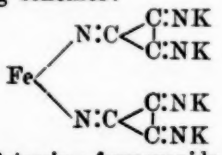


the metals iron and potassium being attached directly to carbon atoms.

Etard and Bémont (*Compt. rend.*, 1884, **99**, 972, 1024), and Friedel (*ibid.*, 1887, **104**, 994), suggested a ring formula consisting of six carbon atoms, thus recalling the structure of the benzene ring:

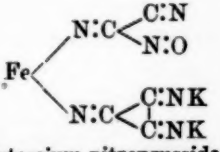


The iron and potassium are here attached to nitrogen, the formula being *iso*cyanic, and this is supported, in so far as the potassium atoms are concerned, by Freund's observations in regard to ethyl ferrocyanide prepared from the silver salt and ethyl iodide (*Ber.*, 1888, **21**, 931). On heating, the ester decomposes, yielding ethyl carbylamine. Browning (T., 1900, **77**, 1234) agrees that the *iso*cyanide formula is most probably correct, but takes exception to a ring structure in view of the fact that the formation of nitroprussides takes place readily in practice, whereas in theory it necessitates the rupture of the ring. He therefore suggests the following schemes:



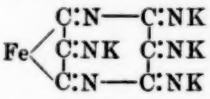
Potassium ferrocyanide.

and



Potassium nitroprusside.

None of these formulæ, however, accounts for the fact that the potassium atoms are labile, whilst the iron atom is not. Denigès (*Bull Soc. chim.*, 1916, **20**, 79) overcomes this difficulty as follows:



This formula has two points in its favour, namely:

(1) In common with Browning's formula, it admits of the ready formation of nitroprussides.

(2) Since the iron atom is not attached in the same way as the potassium atoms, a difference in stability may readily be accounted for.

Whilst, however, the formula is consistent with Freund's results, which indicate that the potassium must be attached to nitrogen, it ignores the evidence adduced by Browning in favour of the iron being similarly attached.

Finally, in Werner's formula the cyanogen groups are attached directly to the central iron atom, which is specially endowed with a valency of six, whilst the dissociable potassium ions hover round the nucleus. The scheme has thus the same disadvantages as those suggested by Werner for the metalammines, and already discussed.

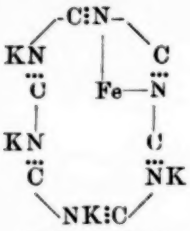
All the foregoing formulæ for potassium ferrocyanide are thus open to objection, and an even more serious discrepancy lies in the fact that not one of the formulæ admits of the possibility of the isomerism of the salt without partly destroying the cyanide or *iso*cyanide constitution, as the case may be.

In 1911 Briggs (T., 1911, **99**, 1019) showed that two isomerides of potassium ferrocyanide are capable of existence. The α-salt is stable in alkaline solution, but in neutral or acid solution it is converted into the β-isomeride. The change is reversible on reversing the conditions. Briggs suggests that these are stereo-isomerides, and represents them by the following schemes:

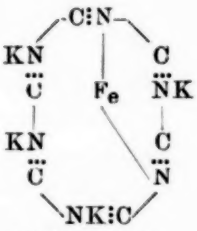
although it is impossible at present to determine which scheme corresponds with the α- or β-form.

If the cyclic theory of the present author is accepted, how-

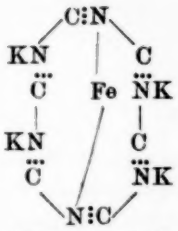
ever, all the above difficulties disappear. Three formulæ are possible, namely:



Ortho- or 1 : 2-ferrocyanide.



Meta- or 1 : 3-ferrocyanide. (α-Salt.)



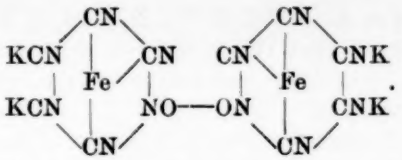
Para-, s- or 1 : 4-ferrocyanide. (β-Salt.)

In the above schemes the potassium atoms are attached, not to the central iron atom, but to the ring itself, so that isomerism becomes possible according to the positions assumed by these atoms. It will be observed that the ortho-form is simply the double salt $4KCN,Fe(CN)_2$, and in view of the instability of ferrous cyanide it is possible that the complex may not be very stable either. The meta- and para-salts are more evenly balanced, and may be expected to exhibit greater stability. It is reasonable, therefore, to suppose that these correspond with the two known isomerides.

In each formula both the iron and potassium atoms are united to nitrogen in accordance with Browning's observations; nevertheless, the reason for the inability of the iron atom to ionise on its own account is clear. Finally, conversion of either complex into nitroprusside does not involve a rupture of the ring, as is evident from the formula given below, so that Browning's objection to a ring is removed.

The problem now is to determine which formula corresponds with the α-salt and which with the β.

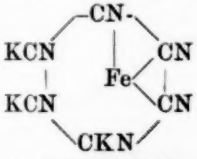
When nitric oxide is bubbled through an acidified solution of potassium ferrocyanide, nitroprussic acid is formed (Playfair, *Phil. Mag.*, 1850, [3], **36**, 197, 271, 348). This acid is only known in one form, and the same is true of its salts. Now consideration of the foregoing formulæ for potassium ferrocyanide shows that whilst the para-form can only yield one nitroprusside, the meta-form should be able to yield two isomerides. Since the reaction takes place in acid solution in which the β-ferrocyanide is stable, it would appear that the α- and meta-salts correspond, and the β- and para-salts. Such being the case, the formula for potassium nitroprusside becomes



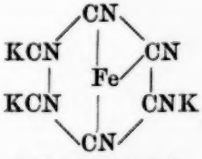
It is important to note that in consequence of the indefinite manner in which the potassium atoms are, in Werner's theory, supposed to hover round the ferrocyanide nucleus, no isomerism of the salt is possible. The theory is thus clearly inadequate. Werner himself tacitly acknowledges this, for in his latest edition of "Neuere Anschauungen, etc." (1913), he includes the ferro- and ferri-cyanides under the heading "Unaufgeklärte Isomerie-erscheinungen."

Potassium Ferricyanide.

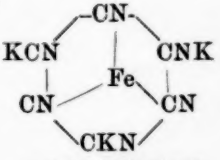
Three cyclic formulæ may likewise be written for potassium ferricyanide, namely:



1 : 2 : 3-Ferri-salt.



1 : 2 : 4-Ferri-salt. (β-Salt.)



s-1 : 3 : 5-Ferri-salt. (α-Salt.)

Of these, the first formula simply represents the double salt $3KCN,Fe(CN)_3$, which is probably unstable, on account of the instability of ferric cyanide. The two other formulæ represent what we might reasonably expect to be stable salts, and correspond with the two isomerides of potassium ferricyanide (Locke and Edwards, *Amer. Chem. J.*, 1899, **21**, 193, 413; Bellucci and Sabatini, *Atti R. Accad. Lincei*, 1911, [5], **20**, i, 176), known respectively as α and β. The latter is stable in acid solution, and is hence derivable from the β- or para-ferrocyanide, so that it is represented by the middle formula above. The α-isomeride is accordingly the 1 : 3 : 5-ferri-salt.

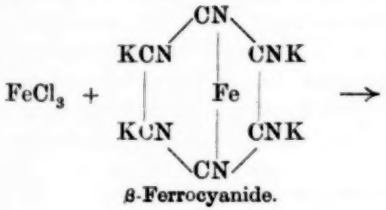
Prussian Blues.

When a solution of potassium ferrocyanide reacts with rather less than one equivalent of a ferric salt, a blue, hydrated precipitate of α-soluble Prussian blue or ferric potassium ferrocyanide, $Fe'''K[Fe''C_6N_6]$, is obtained. A similar blue precipitate results when a ferrous salt reacts with potassium ferricyanide.

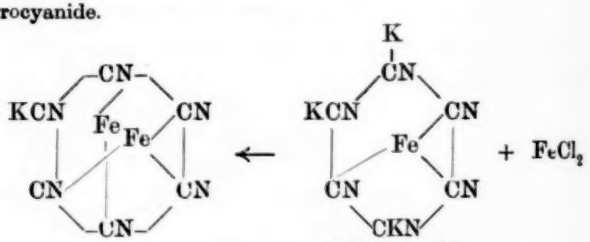
Hofmann and his co-workers (*Annalen*, 1904, **337**, 1) have shown that the two precipitates are identical when prepared under precisely analogous conditions, although in the second case ferrous

potassium ferricyanide, $Fe''K[Fe'''C_6N_6]$, might be expected. It is therefore assumed that the latter salt is unstable, and at the moment of formation undergoes intramolecular rearrangement to the first-named complex.

The difficulty disappears entirely, however, if the cyclic formulæ is accepted. For example, β-potassium ferrocyanide reacts with a ferric salt, yielding 2:3:5-ferric 6-potassium 1:4-ferrocyanide,



β-Ferrocyanide.



β-Ferricyanide.

and this is clearly identical with 1:4-ferrous 5-potassium 2:3:5-ferricyanide obtained by the action of β-potassium ferricyanide on a ferrous salt. Accordingly, no assumption of intramolecular change is necessary to account for the identity of the two precipitates.

Two other stable schemes are possible according to the conditions of precipitation, namely, 2:3:5-ferric 1-potassium 4:6-ferrocyanide and 1:3:5-ferric 6-potassium 2:4-ferrocyanide. These three schemes correspond with the three soluble isomeric Prussian blues that are known.

[ADDENDUM.—Since the above was written the author has been able to consult the original paper by Denigès, which, at the time of writing, was only accessible in short abstract. Some of the formulæ suggested by Denigès are cyclic and somewhat similar to those given above, but the iron atoms are generally assumed to be linked directly to carbon atoms, and it is regarded as of no importance whether the iron atoms be without or within the rings. It is the emphasis laid on the latter point which characterises the present author's views.]

THE VICTORIA INSTITUTE,
WORCESTER.

[*Received, May 23rd,* 1916.]

LXI.—*The Influence of Iron Pyrites on the Oxidation of Coal.*

By Thomas James Drakeley.

The effect of the presence of iron pyrites on the oxidation of coal is a subject on which various opinions are held. Some authorities maintain that its influence is favourable (Meyer, *J. pr. Chem.*, 1872, [ii], **5**, 407; Lamplough and Hill, *T. Inst. Min. Engrs.*, 1913, **45**, 645; Louis, *ibid.*, 651; Hall, *ibid.*, 1914, **46**, 571), some that it has nothing whatever to do with the spontaneous ignition of coal (Threlfall, "Second Report of the Royal Commission on Coal Supplies," 1904 [Cd. 1991], **2**, 227; Lewes, *ibid.*, 232; Lawton, *T. Inst. Min. Engrs.*, 1904, **27**, 112), whilst others regard its presence as detrimental to the oxidation of the coal (Fayol, *Bull. Soc. Ind. Min.*, 1879, [ii], **8**, iii, 3487; Dennstedt and Bünz, *Zeitsch. angew. Chem.*, 1908, **21**, 1825).

It may be recalled that years ago the popular idea was that the spontaneous combustion of coal was due solely to the presence of pyrites in the coal. This theory was overthrown mainly by the classical researches of Richters (*Ding. Poly. J.*, 1868, **190**, 398; 1869, **193**, 54, 264; 1870, **195**, 315, 449; **196**, 317; for summary see Wagner's "Jahresbericht über die Fortschritte der Chemischen Technologie," 1870, **16**, 758) and Fayol (*loc. cit.*), but was brought into prominence again by the investigations of Haldane and Meachem (*T. Inst. Min. Engrs.*, 1898, **16**, 491; compare, however, Harger, *ibid.*, 1913, **44**, 318) and upheld by Jeffries (*T. Inst. Min. Engrs.*, 1905, **29**, 532).

The generally accepted view among coal-mining men at the present time seems to be that little importance is to be attached to the presence of pyrites and that a sufficient explanation of spontaneous combustion is to be found in the rapidity with which coal absorbs oxygen and heats. Interesting information on this point is contained in the Minutes of Evidence (February 12th—July 16th, 1913) given before the Departmental Committee on Spontaneous Combustion in Coal Mines.

Dissemination throughout the rock of carbonaceous matter intimately mixed with finely divided pyrites is regarded as a determining factor in the production of fires in iron mines (compare Higgins, Bureau of Mines, U.S.A., Technical Paper 59), yet despite the fact that the conditions of its occurrence are largely identical with those in a coal mine, many investigators protest

against the inclusion of pyrites even as a contributory factor in coal-mine fires.

A series of experiments was devised therefore to ascertain definitely the effect produced by the presence of iron pyrites on coal. Before conducting the experiments, the question arose as to whether moist or dry air should be the oxidising medium, and on seeking information on this point the conclusions arrived at by various investigators are as conflicting as those given in regard to the question of the iron pyrites. Thus moisture is considered to act as a deterrent to spontaneous combustion by Richters (*loc. cit.*) and the New South Wales Commission, 1896—1900 (see Threlfall's description of the experiments, *J. Soc. Chem. Ind.*, 1909, **28**, 759); Fayol (*loc. cit.*) states that its influence is unobservable; whilst the weight of the evidence given by witnesses before the British Royal Commission, 1876 (inquiring into the causes of spontaneous combustion of coal) is heavily in favour of the opinion that moist coal is more liable to ignite than dry coal (compare letter to Commission from Mr. Poole, Inspector of Mines of Nova Scotia). This view is upheld by Lewes (*loc. cit.*), Mahler (*Ann. des Mines*, 1913, [ii], **4**, 163), and Winmill (*T. Inst. Min. Engrs.*, 1915, **48**, iii, 503). Recently Graham (*T. Inst. Min. Engrs.*, 1915, **49**, 35) has shown that coal-dust when moist absorbs oxygen at a rate approximately half as great again as that of dry dust.

The variety of opinion regarding the influence of moisture seems to be due to the meaning to be attached to the term "dry" coal. Coal containing its natural moisture is, from a chemical point of view, wet, but is considered dry by the New South Wales Commission. In fact, it is doubtful whether the results of the experiments conducted by this Commission are so conclusive that the views of the British Commission, 1876, "must now be definitely abandoned," for the coal used as dry coal contained its natural moisture, amounting to 2·2 per cent., whilst the wet coal was saturated by playing a stream of water on it.

Probably the view held at present in the mining world is correct, namely, that moisture plays an important part in, and accelerates, the oxidation of the coal. It is considered, however, that an excessive amount of water retards spontaneous combustion in two ways. First, the water enters the pores of the coal and so renders it less pervious to the air, and secondly, the temperature is kept low by evaporation.

A moist atmosphere is practically essential for the oxidation of the iron pyrites, and the author judges that it would also be favourable for the oxidation of the coal. With a moist atmo-

sphere the coal would not become unduly wetted or dried, but would retain its natural moisture throughout the experiment.

Experimental.

The experimental work is divided into two sections.

Part I. deals with the influence of iron pyrites on the oxidation of coal to carbon dioxide.

Part II. gives an account of the effect of iron pyrites on the absorption of oxygen by the coal.

Part I.

In order to ascertain the influence of iron pyrites on the oxidation of coal to carbon dioxide, the oxidation products of:

(i) Pyrites;
(ii) Coal;
(iii) An artificial mixture of pyrites and coal;
(iv) Ferrous sulphate;
(v) A mixture of ferrous sulphate and coal;
(vi) A mixture of sulphuric acid and coal,

were determined.

The coal used in the experiment was a specially selected sample of "King" coal from the Pemberton Colliery, near Wigan. In this seam of coal no case of spontaneous combustion has ever occurred.

Owing to the possibility of the coal absorbing oxygen rapidly when freshly mined, this sample was kept from 1913 to 1915. In this way it was thought possible to have eliminated any uncontrollable factor which might have caused a variation in the coal between the experiments.

A complete analysis of the coal was made in 1915.

Ultimate Analysis.

Carbon	76·020 per cent.
Hydrogen	5·076 „ „
Nitrogen	1·364 „ „
Sulphur	1·358 „ „
Ash	4·750 „ „
Oxygen, etc. (by difference)	11·432 „ „
	100·000

Proximate Analysis.

Coke	62·99 per cent.
Ash	4·75 „ „
Moisture	1·329 „ „

Analysis of Ash.

Silica	38·72	per cent.
Alumina	25·15	,, ,,
Iron sesquioxide	21·87	,, ,,
Sulphate (SO_4)	6·71	,, ,,
Lime	3·96	,, ,,
Magnesia	trace	
Undetermined constituents	3·59	,, ,,
	100·00	

Specific gravity of coal = 1·280

The pyrites was a selected sample and was free from carbonates.

Analysis of the Pyrites.

Silica	1·20	per cent.
Iron	46·38	,, ,,
Sulphur	51·84	,, ,,
Copper	trace	
	99·42	

Specific gravity of pyrites = 4·97

The analysis of the pyrites showed an excess of 1·02 per cent. of iron, and if it is assumed that this excess is present in the pyrites as the sesquioxide, an additional 0·44 per cent. of oxygen is introduced. This would bring the total for the analysis to 99·86.

A finely divided sample of the pyrites was exposed to the air of the laboratory for three months. A microscopic examination then showed that about one quarter of the powder was completely oxidised, whilst the remainder still retained the brassy lustre. The pyrites therefore seemed to be mixed, so far as its resistance to the oxidising action of the air was concerned.

The apparatus in which the oxidation was carried out was of the form of a large horizontal condenser, and consisted of a glass tube ($140 \times 3{\cdot}75$ cm.) surrounded by an iron tube (125×5 cm.) as jacket. Steam was passed through the annular space between the two tubes.

Fifty grams of the material for oxidation were placed in the spaces between five wet glass-wool plugs, which were introduced to keep the air moist during its passage through the inner tube. The air was drawn through the tube by means of a filter pump at the rate of about $1\frac{1}{2}$ litres per hour, and was freed from carbon dioxide and sulphur dioxide before entering. On leaving the inner tube, the air bubbled through three absorption bulbs containing potassium hydroxide, in which the carbon dioxide and

sulphur dioxide resulting from the oxidation of the material in the tube were collected.

During the experiments, each of which occupied thirty-six hours, steam was blown through the iron jacket, with the result that the temperature of the air leaving the inner tube varied from 36° to 39°, having entered at 15—18°.

At the close of each experiment the contents of the tube and the absorption bulbs were tested for oxidised products. The results were corrected for the "blank" estimations which were made in all possible cases.

In experiments (i) to (iii) the oxidised iron and sulphur in the residue in the tube were extracted with air-free, dilute hydrochloric acid, whilst in experiments (iv) to (vB) the amount of iron oxidised to the ferric state was estimated volumetrically, and is given as a percentage of the total iron present.

The results, calculated for the specified weights of the substances, are tabulated below.

Experiment	i.	ii.	iii.	iv.	vA.	vB.	vi.
Substances for oxidation.	100 Grams of pyrites.	100 Grams of coal.	Mixture of 100 grams of pyrites and 100 grams of coal.	100 Grams of ferrous sulphate.	Mixture of 100 grams of coal and 100 grams of ferrous sulphate.	Mixture of 100 grams of coal and 5·26 grams of ferrous sulphate.	Mixture of 100 grams of coal and 10 c.c. of dilute sulphuric acid (1 in 10).
	Gram.	c.c.	Gram.	Per cent.	Per cent.	Per cent.	c.c.
Iron oxidised ...	0·6510	—	0·5240	82·39	79·68	52·79	—
Sulphur oxidised to SO_4..... ...	0·5730	—	0·3225	—	—	—	—
Sulphur oxidised to SO_2	0·1405	—	0·2786	—	—	—	—
Total sulphur oxidised	0·7135	—	0·6011	—	—	—	—
			c.c.		c.c.	c.c.	
Carbon dioxide.	—	24·17	82·8	—	8·17	45·6	18·8

Discussion of the Results.

(i) In this experiment it would be expected that if 0·7135 gram of sulphur of the iron pyrites were oxidised, 0·6243 gram of iron would become soluble in the acid. The amount actually determined was higher. This may be due to the pyrites becoming more finely divided, so that a larger quantity of the excess of iron (1·02 per cent.) in the pyrites would be available to the action of the acid than in the blank determination on the ordinary sample.

An analysis of the solution extracted with the air-free, dilute hydrochloric acid from the pyrites left in the tube indicated the presence of almost pure ferric sulphate.

From this it may be concluded that under the conditions of the experiment and in the absence of carbonaceous matter the pyrites oxidises to form ferric sulphate.

(ii) No oxidation of the iron and sulphur, which occur naturally in the coal in small quantities, could be detected.

(ii and iii) The analysis of the solution extracted in experiment (iii) indicated that the oxidation of pyrites under the conditions of the experiment and in the presence of carbonaceous matter is mainly to give ferrous sulphate.

The most notable point was the increase in the evolution of carbon dioxide from 24·17 c.c. to 82·8 c.c. The liberation of carbon dioxide seemed peculiar, for some investigators (compare Parr and Kressmann, Bulletin No. 46, University of Illinois) state that there is no liberation of oxidised gaseous products from coal until the temperature reaches 100° or above. Contrary views are also held (compare Cox, *Philippine J. Sci.*, 1912, **7**, 297; Winmill, *T. Inst. Min. Engrs.*, 1914, **46**, 563). It may be noted that the portion of the coal in contact with the tube might have its temperature raised to this value, although the temperature of the air passed over it never exceeded 39°.

Another point to be noted is that in the experiment with the pyrites alone, more of this mineral was oxidised than when it was mixed with coal. This may be due to two factors: first, the coal may have exercised a deterrent effect by absorbing the oxygen; secondly, the ventilation of the mixture may not have been so effective, for the volume of 50 grams of the mixture exceeded the volume of the same weight of powdered pyrites.

(iv and v) These experiments were conducted in order to determine whether the iron compounds produced by the oxidation of the pyrites caused an increase in the volume of carbon dioxide liberated.

In experiment (VA) a small volume was obtained, but this was probably due to the fact that after a few hours the coal was saturated, and was finally submerged. The experiment was repeated (VB) with a mixture containing 5 per cent. of ferrous sulphate, and from this mixture the volume of carbon dioxide collected rose to 45·6 c.c., whilst the percentage of iron oxidised to the ferric state only reached 52·79. Again, in this experiment the coal appeared moist after about twenty-nine hours, but the result seems sufficient to show that the ferrous sulphate increases the liberation of carbon dioxide by the coal.

(vi) The results of this experiment indicate that any sulphuric acid produced by the oxidation of the pyrites would not aid in the production of carbon dioxide. The volume of carbon dioxide liberated in this case was far below that obtained from the coal alone. This may be due to the dilute sulphuric acid filling the pores, and thus preventing the oxygen of the air from penetrating the coal-dust.

PART II.

Experiments were conducted to determine how the admixture of iron pyrites, ferrous sulphate, and sulphuric acid with the coal influenced its absorption of oxygen.

Six large flasks of almost equal volume were clamped horizontally and fitted with rubber stoppers, through which passed glass tubes 120 cm. long. These were bent at right angles 10 cm. from the flask and their ends dipped under water so that the absorption of oxygen could be measured by the rise of the water up these tubes. Had the absorption proved large, the ends could be immersed in mercury so that the flasks should not be flooded with water. The absorption of oxygen by the sample of "King" coal, however, was exceptionally small; incidentally, this may account for the fact that no case of spontaneous ignition has occurred in this seam.

Into five of the flasks were placed 50 grams of the following powders: "King" coal, iron pyrites, a mixture of equal weights of iron pyrites and coal, ferrous sulphate, and a mixture of coal with five per cent. of ferrous sulphate, whilst the sixth flask contained a mixture of 50 grams of coal with 5 c.c. of dilute sulphuric acid (1 in 10).

The sample of "King" coal was mined in the morning and brought to the laboratory early in the afternoon. Four large pieces of coal (about 22·5 cm. cube) were broken open and the central portions of about 70 grams were taken from each. This coal was rapidly powdered, sieved, mixed as stated above, and

placed in the flasks. The time taken for this operation amounted to about eleven minutes. An analysis of the sample is given below.

Ultimate Analysis.

Carbon	81·069	per cent.
Hydrogen	5·666	,, ,,
Nitrogen	1·088	,, ,,
Sulphur	1·042	,, ,,
Ash	3·338	,, ,,
Oxygen, etc. (by difference)	7·797	,, ,,
	100·000	

Proximate Analysis.

Coke	62·085	per cent.
Ash	3·338	,, ,,
Moisture	2·269	,, ,,

Specific gravity of the coal = 1·291

A wide boat containing freshly slaked lime was placed in each flask to absorb any carbon dioxide which might be evolved, and to keep the air moist a wet glass-wool pad was introduced into each of the necks of the flasks. At the close of the experiments a test made for methane showed it to be entirely absent.

The volume of air in each of the flasks was determined. Readings of the atmospheric pressure, temperature (which varied from 13·2° to 15·8°), and the level of the water in the tubes were taken every three hours during the daytime for seven days. From these readings the volumes of oxygen absorbed by the specified weights of material were calculated, and are recorded in c.c. in the table on page 731.

In the diagram (p. 732) only the results up to the forty-eighth hour are shown, as from the thirty-sixth hour the graphs become almost straight lines. The curves are obtained by plotting the results as follows: curve I from the results in column (*c*), II from the sum of (*a*) and (*b*), III from (*e*), IV from (*f*), and V from (*b*).

Discussion of the Results.

Since curve I rises more rapidly than curve II, it would appear that mixing the iron pyrites with the coal causes the absorption of oxygen to be more vigorous at first. After the absorption of about 34 c.c. of oxygen the two curves become almost parallel straight lines, showing that the iron pyrites has ceased to increase the rate of oxidation.

The course of the oxidation of iron pyrites is first to form

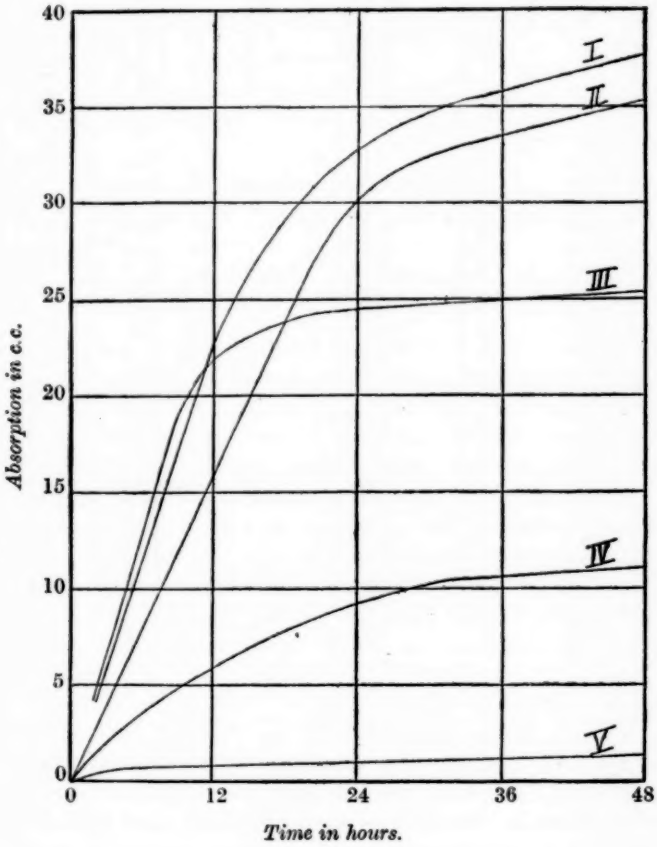
Hours.	(a) 50 Grams of coal.	(b) 50 Grams of iron pyrites.	(c) Mixture of 50 grams of coal and 50 grams of iron pyrites.	(d) 2·5 Grams of ferrous sulphate.	(e) Mixture of 50 grams of coal and 2·5 grams of ferrous sulphate.	(f) Mixture of 50 grams of coal and 5 c.c. of dilute sulphuric acid (1 in 10).
3	3·8	0·3	6·1	—	6·5	2·5
6	7·5	0·7	11·1	—	12·0	3·3
18	23·2	0·8	29·3	—	23·9	8·1
21	26·2	0·9	30·9	—	24·5	8·7
24	29·0	1·0	32·5	—	24·6	8·9
27	30·5	1·0	34·0	0·05	24·7	9·9
30	31·8	1·2	35·0	—	24·8	10·3
42	33·1	1·4	36·6	—	25·1	11·0
45	33·2	1·5	37·1	—	25·3	11·0
48	33·5	1·5	37·6	0·01	25·5	11·3
51	33·6	1·6	37·9	—	25·6	11·4
54	33·8	1·7	37·9	—	25·7	11·5
66	34·8	2·1	39·5	—	26·0	11·7
69	35·0	2·2	39·7	—	26·1	12·0
72	35·3	2·2	40·2	—	26·3	12·4
75	35·5	2·3	40·3	—	26·5	12·5
78	35·6	2·5	40·7	0·15	26·5	12·5
90	36·3	2·7	41·6	—	27.0	12·6
93	36·7	2·8	42·2	—	27·0	12·6
96	36·7	2·9	42·4	—	27·0	12·7
99	37·0	3·0	42·6	—	27·1	12·8
102	37·2	3·0	42·9	—	27·5	12·9
114	38·2	3·4	44·1	—	28·0	13·4
120	38·6	3·5	44·8	0·2	28·1	13·5
144	40·3	4·2	47·0	0·25	28·8	14·6
168	41·2	5·0	49·1	0·3	29·7	15·2

ferrous sulphate and finally to give ferric sulphate. Richters' suggestion that the ferric sulphate is reduced by contact with the coal seems feasible, for by alternate oxidation and reduction the iron may act as an oxygen carrier to some particular compound in the coal. When this compound is oxidised, the iron ceases to possess catalytic properties and the oxidation becomes an additive process.

Another point in connexion with this suggestion is that apparently the most readily oxidised material of the coal is the one to which the iron behaves as an oxidising agent. (For the catalytic effect of ferruginous compounds in coal, compare Dennstedt and Hassler, D.R.-P., 203848.)

If it is assumed that the presence of iron compounds increases

the rate of oxidation (compare von Meyer, Lamplough, and Hill, *loc. cit.*), it is difficult to explain satisfactorily the curve III. At first the oxidation took place the most rapidly, but then fell off to a slower rate than for coal alone. This peculiarity may be due to the fact that the ferrous sulphate tended to cause the



mixture to form into a cake, and thus may have considerably reduced the rate of absorption of oxygen.

Curve IV indicates that sulphuric acid is a deterrent to the oxidation of the coal. An explanation of this may be that the coal, by being moistened with the acid, was rendered less pervious to the air, and therefore the absorption proceeded at a slower rate.

Conclusion.

Iron pyrites has a minor effect (compare Porter and Ovitz, Bureau of Mines, U.S.A., Technical Paper 16), but because coals which cannot be regarded as pyritic are among those most liable to spontaneous ignition (compare Commission of the New South Wales Government, 1896—1900; *T. Inst. Min. Engrs.*, 1900, **19**, 546) it cannot be inferred that its presence may be ignored.

It is very difficult to draw any conclusions from the percentage of sulphur which a coal contains, for pyrites disseminated throughout the coal in microscopical particles will act more effectively than larger quantities of nodular pyrites.

To make any inferences from the analyses of coals from various collieries, even though the samples be from the same seam, is almost impossible, for great differences may exist in the physical conditions under which the coal occurs. Any one of these conditions, for example, a fault or a poor roof, may have a more predominating influence on the question of the ignitibility of the coal than its percentage of sulphur. It is therefore with the view of drawing no conclusions that the author points out that in the majority of cases of spontaneous combustion mentioned in the Minutes of Evidence (February 12th—July 16th, 1913) given before the Departmental Committee on Spontaneous Combustion in Coal Mines, in which the pyrites question is broached, this mineral is stated to be found in the finely disseminated form.

The results of the experiments appear to indicate that pyrites, although a subsidiary factor, is not entirely negligible. A protest therefore may be made against the common practice of disregarding the influence of pyrites on the spontaneous ignition of coal.

In concluding, the author wishes to express his thanks to E. B. Naylor, Esq., Head of the Chemistry Department, and to G. Hunter, Esq., Head of the Mining Department, for the interest they have shown during the course of the experiments.

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WIGAN.

[*Received, May 5th*, 1916.]

LXII.—*The Coagulation of Colloidal Arsenious Sulphide by Electrolytes, and its Relation to the Potential Difference at the Surface of the Particles.*

By Frank Powis.

From a study of the relationship between the stability of an oil–water emulsion and the potential difference at the oil–water interface (P.D. will henceforth be used for the potential difference at the interface of the water and suspended particles), the author was led to conclude that the emulsion was comparatively stable whenever the P.D. exceeded a certain value (positive or negative), but coagulated whenever it was below this critical value (*Zeitsch. physikal. Chem.*, 1914, **89**, 186). It was also pointed out that the only suitable data regarding the relationship between the stability of colloidal solutions and the P.D., namely, those of Burton (*Phil. Mag.*, 1909, [vi], **17**, 583) indicated that the same held good for colloidal solutions, although Burton did not interpret them in this way. When starting the following experiments the author's intention was to test this idea in the case of several colloids, but since it is doubtful whether there will be opportunity to carry this work further, it seems advisable to publish the results already obtained.

A colloidal solution of arsenious sulphide was prepared by Freundlich's method (*Zeitsch. physikal. Chem.*, 1903, **44**, 129). Washed hydrogen was passed through it until it had almost no odour of hydrogen sulphide. It was then filtered, very little solid being retained by the filter. The resulting colloidal solution contained about 11 grams of arsenious sulphide per litre, and had a conductivity of 5×10^{-5} mho. at 17°. Before use, it was diluted with an equal volume of distilled water, the conductivity then being 4×10^{-5} mho., indicating that a large proportion of the electrolyte present was adsorbed on the particles. Only a small portion was diluted at one time, since the more concentrated solution kept better, perhaps simply because the bottle was not opened so frequently.

Coagulation Observations.

In determining the influence of electrolytes on the stability, 5 c.c. of the (diluted) colloidal solution were placed in a well-steamed test-tube and 5 c.c. of electrolyte solution of the requisite concentration added. The tube was immediately reversed twice so as to mix the contents, and the appearance then noted. It was

then allowed to remain, and the appearance again noted at suitable intervals. As there seems to be no description on record of the appearance presented when gradually increasing amounts of electrolyte are added to colloidal arsenious sulphide, or, so far as the author is aware, any colloid, and of the changes which occur on keeping or on shaking, the following observations with barium chloride may be given as typical. The concentration is in millimols. per litre in the final colloid–electrolyte mixture.

Concentration.	Appearance.
0·3 and all below	No turbidity either immediately or after twenty-four hours.
0·4	No immediate turbidity. After five hours no precipitate was present, but the whole of the liquid was turbid. After remaining undisturbed until the next day, the liquid was still turbid throughout, but on disturbing, some small flakes became visible, which slowly settled to the bottom. Most of the arsenious sulphide, however, still remained in such small particles or groups of particles that after again remaining undisturbed for twenty-four hours the liquid was turbid up to the top.
0·5	Very slight turbidity was noticeable after a few minutes. After one hour it was very turbid. After five hours there was a layer of clear liquid about 1 cm. deep at the top; no distinct precipitate was visible, perhaps because of the turbidity of the liquid. After remaining undisturbed for a day the precipitate still occupied a fairly large volume, but the liquid above was clear and colourless. On disturbing gently, the gel-like precipitate broke up into large flakes which settled rapidly and occupied a much smaller volume than before.
0·6	Became very turbid within a few minutes. It was disturbed again, when small flakes formed which settled slowly. After then remaining undisturbed for a day almost all the arsenious sulphide had separated in the precipitate, but the liquid above was slightly cloudy. (The cloudiness in this case, whereas the liquid in the preceding case is given as being clear, is due to the liquid being shaken, as will be described later.)
0·7	No distinct turbidity was produced immediately, but the liquid became very turbid within a few minutes. It was then disturbed again, when large flakes formed which settled fairly quickly. After remaining for twenty-four hours all the arsenious trisulphide was precipitated and the liquid above was quite clear.
0·8 and higher concentrations.	Became turbid when the electrolyte solution was poured in, and on reversing the tube so as to mix the contents, large flakes formed which settled rapidly. The liquid above was rather cloudy at first, but after twenty-four hours it had become quite clear.

After the first day the only mixtures showing any appreciable change compared with the mixture of 5 c.c. (diluted) colloid + 5 c.c.

water were those with concentrations between 0·4 and 0·6 millimol. per litre, and in these the change was very slow. After four days the liquid in the 0·6 tube had become quite clear, and that in the 0·5 tube was only slightly cloudy, but the 0·4 mixture was still yellow and turbid, and only a small amount of precipitate had settled at the bottom. This 0·4 millimolar mixture slowly underwent further change, so that after eight days nearly all the arsenious sulphide had settled to the bottom, but the liquid was still turbid, with a yellowish-white appearance; after thirty-two days the liquid was only slightly cloudy, and had a bluish-white tinge. The difference in the light reflected from the mixture as it changed from turbid through cloudy to almost clear, is no doubt due to the settling of the larger particles, so that the average size of those remaining suspended gradually decreased.

After two months the mixture containing 0·3 millimol. per litre was still like the pure colloid; both contained a very small amount of precipitate, and appeared almost clear in transmitted light, but turbid in reflected sunlight; the yellow colour of both was much less intense than at first, probably due to slow chemical action, for example, hydrolysis of the arsenious sulphide.

Examination of the above observations shows that there is no definite concentration above which coagulation occurs almost immediately, but below which no coagulation occurs. Yet the limits of concentration for these are fairly narrow, being below 0·8 but above 0·3 millimol. per litre. Odén (*Zeitsch. physikal. Chem.*, 1912, **78**, 682) obtained results with colloidal sulphur which are important in this respect. He found that when all the particles in the colloidal solution were of approximately the same size, the concentration at which coagulation occurred was much more sharply defined than when particles of widely different size were present. Moreover, the smaller the size of the particles in these solutions the larger was the concentration of electrolyte necessary for coagulation, indicating that the larger particles of any colloidal solution coagulate more easily than the small ones. Galecki (*Zeitsch. anorg. Chem.*, 1912, **74**, 174) has shown that in the coagulation of gold sols. the larger particles act as nuclei for the smaller ones. The presence of particles of very different size is therefore probably the reason why the coagulation concentration with arsenious sulphide is not very sharply defined.

In determining the influence of electrolytes on the stability of colloids the usual method has been to add the requisite number of drops of a concentrated solution of the electrolyte. This would appear to be very unsatisfactory, since even if this is done in a flask which is shaken, some of the colloidal particles must for a

small interval of time be in contact with an electrolyte solution of much higher concentration than that finally present. This may cause part of the colloid to coagulate, and according to Galecki's results the groups of particles so formed would tend to act as nuclei for the deposition of the remaining particles; so coagulation might occur at a concentration less than the real coagulation concentration. Such a possibility can, however, be almost eliminated by the use of an electrolyte solution not much more concentrated than that required in the final mixture, and running it in slowly while shaking the flask containing the colloidal solution. (In investigating the effect of an electrolyte like thorium chloride in sufficient concentration to reverse the sign on the colloid, it is better to add the colloid to the electrolyte.)

Influence of Shaking.—If equal quantities of colloid and electrolyte solutions are mixed in a tube as described above, the progress of coagulation and settling is little influenced by subsequent shaking of the tube unless the electrolyte concentration is near that which causes immediate turbidity but not immediate coagulation and settling, for example, 0·5 millimolar in the case quoted above. At concentrations near this, shaking greatly facilitates, or one might even say is necessary for, the formation of large, separated flakes; these then settle quickly, but leave the liquid above turbid or cloudy owing to the slow settlement of the remaining smaller particles or groups of particles. If, however, a turbid mixture is left undisturbed, no separate coagula are formed, but the surface of the turbidity slowly sinks in the liquid and leaves it clear and free from particles. As an example, a few of the observations made with barium chloride may be quoted. The test-tube was gently shaken for a few seconds at intervals of half an hour for two hours, then of one hour for three hours, then occasionally as indicated on page 738.

The shaken tube had not been disturbed for nineteen hours before making the last observation, and therefore the difference in appearance of the two tubes was not due to re-suspension of the particles by shaking. After a week, the tube not having been disturbed for four days, the liquid in the "shaken" tube was still slightly cloudy, a few very fine particles still remaining suspended.

With a concentration of 0·8 millimol. per litre or higher than this, large flakes tend to be formed during the initial shaking adopted to mix the two solutions, so that without subsequent shaking the behaviour approximates to that in the tube containing 0·6 millimol. per litre which was shaken at intervals. There was evidence, however, that this would not have been so if the initial shaking had been less vigorous.

Concentration of Barium Chloride, 0·6 millimol. per litre.

Time after mixing	Appearance. Tube shaken	Tube not shaken except the reversal immediately after adding the electrolyte.
Immediately	Turbid	Turbid.
Two hours	Much precipitate at bottom; rest turbid	Layer of clear liquid at top, about 1 mm. deep; rest very turbid. No distinct precipitate at bottom.
Five hours	Large precipitate; liquid above slightly turbid	Some precipitate at bottom. Liquid at top clear for about 7 mm. Rest very turbid, but no separate particles visible.
One day	Dense precipitate containing almost all the arsenious trisulphide. Liquid above slightly turbid except 1 mm. at top.	All the arsenious sulphide contained in precipitate of small bulk. Liquid above quite clear.

With 0·5 millimol. per litre the results were similar in character to those with 0·6. With a 0·4 millimolar solution the two tubes had almost the same appearance when examined after various intervals of time up to a week. After five hours both had become turbid, but gentle shaking did not cause large coagula to form as it did with the turbid 0·6 millimolar solution.

During the first few days the arsenious sulphide in the 0·5 and 0·6 millimolar solutions which were not disturbed after they had once been thoroughly mixed, resembled gelatinous precipitates like ferric hydroxide, and the existence of a honeycomb or network structure would explain the carrying down of the very fine particles which occurred under these conditions, but not when the tube was frequently shaken.

The Relation between the Stability and the Potential Difference at the Surface of the Particles.

In determining the value of the P.D. the method employed by Burton (*Phil. Mag.*, 1906, [vi], **11**, 425) was used. For this a clear solution is required for the upper half of the U-tube, which has a conductivity equal to that of the colloid–electrolyte mixture in the lower half. Moreover, the kind and concentration of the electrolyte or electrolytes present must be the same, although this has not always been attended to.

The simple method adopted for attaining this is illustrated by the following for the determination in presence of 0·05 millimolar aluminium chloride. For the lower half of the tube 50 c.c. of 0·1 millimolar aluminium chloride solution were added to 50 c.c. of (diluted) colloid. For the upper liquid 25 c.c. of 0·2 millimolar aluminium chloride were added to 25 c.c. of undiluted colloid (having, therefore, twice the concentration of the 50 c.c. used above and of that used for the stability determinations). After remaining undisturbed for a few minutes the mixture was shaken and then filtered. In this mixture the concentration of aluminium chloride is sufficient to cause coagulation, and by waiting for some time before shaking, the very small particles stick to or are entangled amongst others, and so a colourless, clear filtrate is obtained. Neglecting the first portion, the rest was diluted with an equal volume of water. It will readily be seen that the concentration of both the aluminium chloride and any electrolyte contained in the colloidal solution will be the same as in the colloid–electrolyte solution used in the bottom half of the tube, or, at any rate, very nearly so, whereas a pure 0·05 millimolar aluminium chloride solution would have a much smaller conductivity.

Table I contains the results of determinations made in the presence of four different electrolytes, the cations of which varied in valency from one to four. For each electrolyte a series of stability determinations was made similar to that given earlier for barium chloride, and the concentration used for the P.D. determination was that at which the colloid had the same stability (or instability) as in presence of 0·5 millimolar barium chloride, that is, the lowest concentration at which rapid coagulation occurred.

TABLE I.

Electrolyte.	Concentration millimols. per litre.	P.D. in volt.*
Potassium chloride	40·0	0·044
Barium chloride	0·5	0·026
Aluminium chloride	0·05	0·025
Thorium nitrate	0·05	0·027
	0·07	0·026
	0·1	0·024

* Arsenious sulphide is a so-called negative colloid, since, as usually prepared, the particles travel towards the anode in an electric field. According to the usual nomenclature, all the P.D. values given in this paper should therefore be preceded by the negative sign, except the value +0·03 volt for ferric hydroxide on p. 741, and +0·03 volt for arsenious sulphide on p. 742, where the + is inserted for distinction.

With regard to stability, the behaviour of the colloid towards thorium nitrate was a little different from its behaviour towards

the other electrolytes tried. With 0·05 millimol. per litre there was no turbidity even after twenty-four hours, but with 0·06 there was immediate turbidity and formation of small flakes. These small flakes settled slowly, but instead of leaving the liquid quite clear and colourless, as might have been expected from the behaviour with barium chloride, the liquid remained yellow and like the pure colloid in appearance. In the presence of 0·1 millimol. per litre the behaviour was very similar, although 0·2 millimol. did cause the formation of large flakes, and after a few hours the liquid above was quite clear and colourless. On comparison with barium chloride, it will be seen that there is a much smaller change in concentration with thorium nitrate in passing from that which does not cause turbidity in twenty-four hours to that which causes immediate turbidity, but a greater change in passing from this to the concentration which causes the liquid to become quite clear and colourless in a few hours. The reason for this difference in behaviour was not ascertained; one would certainly not expect the use of the nitrate instead of the chloride to have this effect. On account of this difference in behaviour, potential measurements were made with 0·05, 0·07, and 0·10 millimol. per litre, the concentration having a coagulative effect equal to that of 0·5 millimolar barium chloride being certainly within this range.

The concentrations of the four electrolytes having equal coagulative effect, as given in table I, by no means form the geometric series which is often said to hold for the coagulation of negative colloids by electrolytes having cations of different valency—a point which was discussed in a previous paper (*loc. cit.*, p. 734).

The P.D. with the "pure" colloid was not determined owing to the difficulty of obtaining for the upper part of the U-tube a solution fulfilling the conditions previously mentioned; one attempt to obtain this by dialysis against distilled water resulted in coagulation before the conductivities of the colloid and outside water became equal. Many such determinations by different observers with other colloids have all given values less than 0·8 volt (for table, see Burton, "The Physical Properties of Colloidal Solutions," p. 135); with a pure oil emulsion the present author found (−)0·046 volt, the highest value in the presence of any concentration of potassium ferrocyanide, which is very powerful in increasing the charge on a negative colloid, being (−)0·07 volt. We may therefore safely conclude that the value for the "pure" arsenious sulphide would be less than 0·1 volt, and probably less than 0·06 volt.

The values given above for the P.D. at the concentration of each electrolyte which is just sufficient to cause rapid coagulation, all

exceed 0·02 volt. They therefore confirm the conclusion drawn by the author (*loc. cit.*, p. 734) from the behaviour of an oil emulsion that the "coagulation concentration" is not that at which the P.D. becomes zero, that is, the isoelectric point, but is much lower, and that here the P.D. has still a relatively high value. As further evidence in support of this, I may mention that a sample of positive colloidal ferric hydroxide coagulated rapidly in the presence of 0·4 millimolar sodium sulphate, although the value of the P.D. at this concentration was +0·03 volt.

With regard to the further question of whether the colloidal solution is stable when the P.D. has a value exceeding a certain critical value, but coagulates if it is below this, the determinations yet made do not allow quite definite conclusions to be drawn. Certainly the figures in the above table for the mean results with barium chloride, aluminium chloride, and thorium nitrate agree quite well with each other, better, in fact, than the separate values for the same electrolyte, as seen from the appendix. The value for potassium chloride, however, is distinctly higher. With hydrochloric acid the coagulation concentration was 30 millimols. per litre, and a single P.D. determination at this concentration gave a value 0·050 volt, and therefore, considering only one determination was made, within the limits of error for the value for potassium chloride.

In dealing with an oil emulsion it was only after taking into account the slow change which occurs in the value of the P.D. when an emulsion containing electrolyte is allowed to remain, that a relationship was found between the P.D. and the stability. The coagulation of the colloid in the presence of 40 millimolar potassium chloride could not, however, be explained in this way, since in some cases the colloid had coagulated to a large extent before the determination was finished. In order to be certain, however, a determination was made with a mixture which had been kept six hours. By this time most of the arsenious sulphide had settled out, but sufficient of the finer particles remained suspended to make the division in the U-tube easily visible. The value obtained was 0·044 volt (first value 0·043, second 0·045), which agrees with the mean of the four determinations made soon after adding the potassium chloride. Consequently, if any change does occur on keeping, it is very slow, and would not explain the high value given for potassium chloride in table I.

The results, therefore, agree with the idea of a critical P.D. as determining the stability or instability of a colloidal solution in so far as barium chloride, aluminium chloride, and thorium nitrate are concerned, but the behaviour with potassium chloride suggests

that electrolytes also exert a kind of salting out effect, so that when an electroyte is used which has only a weak influence on the P.D., and therefore a relatively high concentration is required for coagulation, this coagulation occurs when the P.D. has a value so high that without this superimposed salting out effect the mixture would be quite stable. Since such an effect was not observed in the author's experiments with an oil emulsion where the number of suspended particles per unit volume was very small compared with the number in the colloidal arsenious sulphide, and also does not appear to have occurred to any appreciable extent in Burton's determinations (*loc. cit.*, p. 734), it is perhaps only important when the concentration of the suspended particles is very large. Further experimental investigation is necessary, however, before definite conclusions can be drawn regarding the cause of the value found for potassium chloride being much higher than the values for the other three electrolytes, which agree closely with each other.

The fact that negative colloids coagulated by salts with a univalent cation pass into the colloidal form again on washing away the electrolyte much more readily than when salts with cations of higher valency are used, may be connected with the difference in the P.D. values found above for the two classes of electrolyte.

So far as the stability of a colloidal solution is determined by the P.D. having a value greater than a certain critical value, the lack of sharpness in the coagulation concentration will be due to the critical value being slightly different for particles of different size, Odén's results indicating that the smaller the particle of any one colloid the smaller the value of the critical P.D. In the oil emulsion the limits of size of the particles were only about 1 to 6.

According to the views advanced by the author (*Zeitsch. physikal. Chem.*, 1914, **89**, 91; T., 1915, **107**, 818), addition of sufficient thorium nitrate should cause the P.D. at the surface of the arsenious sulphide particles to become positive, and this was found to be so. For instance, in presence of a 0·5 millimolar solution the value was +0·03 volt. Although this exceeds (numerically) the value given above for the coagulation of the negative arsenious sulphide, namely, 0·026 volt, no range of concentration was found in which the arsenious sulphide was present as a stable positive colloid, even although the arsenious sulphide was added to the thorium nitrate solution. This was no doubt due to the particles adhering before the two solutions had time to mix sufficiently to give 0·5 millimolar thorium nitrate in contact with all the arsenious sulphide particles; in support of this it was observed that although most of the sulphide coagulated and settled almost immediately,

yet a small amount remained suspended, and the upper liquid did not clear anything like so rapidly as with a concentration of 0·1 millimol. per litre; moreover, this was more marked when the colloid was added to the electrolyte than when they were mixed in the opposite order. It is therefore probable that if the colloidal arsenious sulphide had been considerably diluted and slowly run into a flask containing the thorium nitrate, with constant shaking, instead of mixing in a test-tube, it would have been possible to convert it to a positive colloid without coagulation.

Appendix.

In calculating the P.D., the usual formula, $e = \frac{4\pi\eta\mu}{H.D.}$ was used (Freundlich, "Kapillarchemie," p. 229), D being taken as 81, and η as the viscosity of pure water at the temperature during the determination.

Each value given in the following table is calculated from the mean velocity of the dividing surface up one limb and down the other, the latter being generally slightly greater than the former. The current was then reversed, and a second value thus obtained.

TABLE II.

Electrolyte.	Concentration in millimols. per litre.	P.D.			Remarks.
		First value, volt.	Second value, volt.	Mean value, volt.	
Potassium chloride	40·0	0·054	0·037	0·044	
		0·054	0·036		
		0·046	0·041		
		0·045	0·041		With copper sulphate.
Barium chloride	0·5	0·0275	0·027	0·026	
		0·022	0·029		
Aluminium chloride	0·05	0·022	0·027	0·025	
		0·021	0·030		
Thorium nitrate	0·05	0·025	0·041	0·027	With thorium nitrate, after reversing the current the division going down the tube moved abnormally quickly; hence the high value for the second determination, which has been neglected in taking the mean.
		0·029	0·034		
	0·07	0·022		0·026	
		0·030			
	0·1	0·025	0·042	0·024	
		0·023			

Often the colloid had coagulated to a fair extent before the end of the measurements, but sufficient remained suspended to mark the division. The line of division did not always remain quite horizontal, and since the total distance traversed was usually only 0·4 cm., this may introduce an appreciable error. The results obtained are given in table II.

For the determinations with potassium chloride the U-tube was immersed in water. The rise in temperature during the determination was thus reduced to less than 2°. With the lower concentrations required for the other electrolytes the heating effect of the current was only small. In order to be certain that the higher values obtained with potassium chloride were not due to contamination of the liquid near the particles by the products of electrolysis, although the electrodes were 4 cm. away, a determination was made in which above the potassium chloride layer was one of copper sulphate–sulphuric acid solution of the same conductivity, copper electrodes being immersed in it (platinum ones being used for the other determinations), but as seen in the table the same value was obtained.

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LEEDS.

[*Received, June 23rd,* 1916.]

LXIII.—*Some Xanthone Derivatives and Xanthone Colouring Matters.*

By SURENDRANATH DHAR.

THE original object of this investigation was to prepare some colouring matters from xanthone. This substance can be obtained easily and cheaply, and it was thought that it might form a suitable starting point for the preparation of vat dyes. Especially on account of the resemblance between xanthone and anthraquinone it was thought that bimolecular vat dyes might be formed similar to the anthraquinone vat dyes. The positions of the substituents in the known bromo-, nitro-, and amino-derivatives were not the most suitable for the production of interesting vat dyes, and accordingly the preparation of some new substitution products of these simple types was undertaken. Attempts to prepare vat dyes by the condensation of bromo- and amino-derivatives have not yet been successful. Some anilino-derivatives which have dyeing properties have been prepared. Some azo-dyes have also been obtained, but their dyeing properties are of no special interest.

Experimental.

Xanthone.—The yellow colour of xanthone seemed rather unexpected, especially in consideration of the fact that its dinitro-derivatives are almost colourless. On repeated crystallisation from acetic acid or nitrobenzene xanthone was obtained colourless.

Monobromoxanthone.—Graebe prepared this compound by heating it with excess of bromine in sealed tubes (*Annalen*, 1889, **254**, 265), but could not obtain it pure. The following method is more convenient, as it avoids the use of sealed tubes, and readily furnishes the pure compound. Xanthone is dissolved in the least possible amount of hot nitrobenzene in a test-tube, and exactly the theoretical amount of bromine (1 molecule) is added with a trace of iodine. The tube is heated in an oil-bath between 80° and 110° until no more hydrogen bromide is evolved, and finally to 180°. Alcohol is added to the semi-solid product obtained on cooling the tube, the solid is collected, washed with alcohol, and crystallised from benzene. The substance melts sharply at 133° (Graebe gives 125—129°).

Dibromoxanthone.—A. G. Perkin (T., 1883, **43**, 1870) and others have prepared this compound by heating xanthone with bromine in sealed tubes, but this method is found to give the dibromo-compound mixed with other bromo-derivatives from which it could only be separated by very laborious fractional crystallisation. A modified method, similar to that described above for the preparation of the monobromo-derivative, has been worked out, and gives a theoretical yield of dibromoxanthone with very little trouble. Xanthone, dissolved in a small quantity of acetic acid with the theoretical amount of bromine and a trace of iodine, is heated at 110° for one hour. The dibromoxanthone crystallises on cooling the mixture, and is obtained pure on crystallisation from benzene. Bromination may be carried out equally well in nitrobenzene solution under the same conditions. In either of these solvents bromination takes place on allowing the mixture to remain for several days at the ordinary temperature, provided that a trace of iodine has been added. Attempts to prepare tribromoxanthone by direct bromination were unsuccessful.

Tetrabromoxanthone.—This compound was obtained by heating xanthone with four molecular proportions of bromine and a trace of iodine in a sealed tube at 200—275° for six hours; also by heating dibromoxanthone with two molecular proportions of bromine and a trace of iodine under the same conditions for four hours. It was also obtained by heating either α- or β-dinitroxanthone with two to four molecular proportions of bromine in a

sealed tube at 275—290° for eight hours. This displacement of the nitro-groups by bromine atoms was first noticed on attempting to prepare bromonitro-derivatives. It is hoped that this reaction will prove useful in determining the orientation of some of these xanthone derivatives. The substance crystallises in white needles melting at 298°:

0·3408 gave 0·4977 AgBr. Br = 62·15.

$C_{13}H_4O_2Br_4$ requires Br = 62·50 per cent.

Hexabromoxanthone.—Xanthone was heated in a sealed tube with a large excess of bromine and a trace of iodine for ten to twelve hours at about 275°, when the hexabromo-derivative was obtained in golden-yellow, needle-shaped crystals. When recrystallised from benzene it melted sharply at 308°. It was also obtained by heating tetrabromoxanthone or α- or β-dinitroxanthone with excess of bromine under the same conditions:

0·1187 gave 0·1988 AgBr. Br = 70·9.

$C_{13}H_2O_2Br_6$ requires Br = 71·4 per cent.

Dinitroxanthones (α- and β-).—A slight modification of the process of nitration already described by A. G. Perkin (*loc. cit.*) and Graebe (*loc. cit.*) gives both the α- and β-dinitro-derivatives in a pure condition. Xanthone is added gradually, with shaking, to a mixture of equal weights of nitric acid (D 1·4) and concentrated sulphuric acid until a slight precipitate is observed. On allowing the solution to remain for a few hours, shining needles of β-dinitroxanthone are obtained. Mere washing, first with concentrated, then with dilute nitric acid, and finally with water, leaves the substance in a pure condition, It dissolves very sparingly in alcohol and freely in toluene or nitrobenzene and melts at 262°. From the filtrate and washings the α-compound is recovered, which crystallises from hot concentrated nitric acid in fine, pale yellow needles melting at 190°.

Nitration of Monobromoxanthone.

Monobromodinitroxanthone, $C_{13}H_5O_2(NO_2)_2Br$.—One part of monobromoxanthone is dissolved with constant stirring in a mixture of 3 parts of nitric acid (D 1·4) and 1·5 parts of concentrated sulphuric acid. On allowing the solution to remain for a few hours a crystalline precipitate is obtained, which on washing, as in the case of β-dinitroxanthone, remains as bright, pale yellow needles melting sharply at 235°. The substance dissolves sparingly in alcohol or benzene, but readily in nitrobenzene:

0·1218 gave 8·6 c.c. N_2 at 30° and 760 mm. N = 7·95.

$C_{13}H_5O_6N_2Br$ requires N = 7·67 per cent.

Monobromotrinitroxanthone, $C_{13}H_4O_2(NO_2)_3Br$.—From the filtrate and washings another solid, much in excess of the dinitro-compound, was obtained. It crystallises from benzene in rhombohedral, yellow plates melting at 262—265°:

0·1210 gave 10·5 c.c. N_2 at 31° and 760 mm. N = 9·80.

$C_{13}H_4O_8N_3Br$ requires N = 10·24 per cent.

Nitration of Dibromoxanthone.

Dibromodinitroxanthone, $C_{13}H_4O_2(NO_2)_2Br_2$.—One part of the dibromo-compound is dissolved by boiling with a mixture of 15 parts of concentrated sulphuric acid and 30 parts of nitric acid (D 1·48). Colourless, crystalline needles were obtained on cooling, which were collected and washed as before. The substance melts and sublimes at 235—237°:

0·1119 gave 6·2 c.c. N_2 at 31° and 759 mm. N = 6·31.

$C_{13}H_4O_6N_2Br_2$ requires N = 6·30 per cent.

Nitration of Tetrabromoxanthone.

Tetrabromodinitroxanthone, $C_{13}H_2O_2(NO_2)_2Br_4$.—One part of tetrabromoxanthone is boiled with 30 parts of concentrated sulphuric acid and 60 parts of fuming nitric acid in a suspended condition for half an hour, when the dinitro-derivative is obtained. It crystallises from nitrobenzene in rectangular plates, and does not melt at 300°:

0·1735 gave 7·6 c.c. N_2 at 33° and 760 mm. N = 4·92.

$C_{13}H_2O_6N_2Br_4$ requires N = 4·65 per cent.

Attempts were made to nitrate hexabromoxanthone, but according to the different proportions of nitric and sulphuric acids the substance either remains quite unaffected or is completely decomposed.

Reduction.

β-Nitroaminoxanthone, $C_{13}H_6O_2(NO_2)\cdot NH_2$.—The β-dinitro-compound was digested on the water-bath with alcohol (about 100 c.c. for each gram of the substance), concentrated aqueous ammonia (20—30 c.c.) was added in two or three portions, and hydrogen sulphide was passed in. At the end of the reaction the colour had become yellowish-brown, and some flocculent precipitate was formed. After filtering off the latter, the solution was evaporated on the water-bath and yielded the main bulk of the product. The whole mass was made into a paste with concentrated hydrochloric acid, diluted with water, boiled for a short time, and filtered off. The nitroamino-compound was precipitated in fine, yellow needles

from the cold clear solution by the addition of dilute ammonia; when recrystallised from alcohol it melted at 265°:

0·1018 gave 9·85 c.c. N_2 at 25° and 763 mm. N = 11·20.

$C_{13}H_8O_4N_2$ requires N = 10·93 per cent.

β-Nitroacetylaminoxanthone, $C_{13}H_6O_2(NO_2)\cdot NHAc$. — β-Nitroaminoxanthone was acetylated in the usual way by dissolving it in acetic anhydride and adding a drop of pyridine. The product was filtered hot and the filtrate poured into water, when greyish-white needles were precipitated overnight. These did not melt at 300°:

0·1351 gave 11·3 c.c. N_2 at 33° and 762 mm. N = 9·36.

$C_{15}H_{10}O_5N_2$ requires N = 9·39 per cent.

Reduction of α-Dinitroxanthone.

α-Nitroaminoxanthone, $C_{13}H_6O_2(NO_2)\cdot NH_2$.—The α-dinitro-compound was reduced in the same way as the β-dinitro-compound by alcoholic ammonium sulphide. The product crystallised from alcohol in yellow needles melting at 204—206°:

0·1124 gave 10·6 c.c. N_2 at 32° and 762 mm. N = 10·61.

$C_{13}H_8O_4N_2$ requires N = 10·93 per cent.

α-Nitroacetylaminoxanthone, $C_{13}H_6O_2(NO_2)\cdot NHAc$.—The α-nitroamino-compound was acetylated in the same way as the β-compound. Pale yellow needles were obtained which did not melt at 300°:

0·1143 gave 9·7 c.c. N_2 at 33° and 762 mm. N = 9·53.

$C_{15}H_{10}O_5N_2$ requires N = 9·39 per cent.

Colouring Matters.

Dibromoxanthone when heated with ten times its weight of aniline and a trace of copper powder gave a blue, crystalline compound melting at 216—218°. On analysis the nitrogen content was found to be too low to correspond with any definite compound.

Dianilinodibromoxanthone, $C_{13}H_4O_2Br_2(NHPh)_2$.—When tetrabromoxanthone was boiled with ten times its weight of aniline and a trace of copper powder for two hours a bluish-black precipitate was obtained, which, when purified by alcoholic extraction, melted at 140—145°. The same compound was obtained when the bromo-derivative was heated in a sealed tube with the same proportion of aniline for four hours at 260°:

0·1268 gave 6 c.c. N_2 at 31° and 766 mm. N = 5·39.

$C_{23}H_{16}O_2N_2Br_2$ requires N = 5·22 per cent.

It gives blue shades on chrome-mordanted wool.

Hexa-anilinoxanthone, $C_{13}H_2O_2(NHPh)_6$.—When hexabromoxan-

thone was heated with fifteen times its weight of aniline and a trace of copper powder for one hour, a black precipitate was obtained which, when purified by alcoholic extraction, melted at 180—183°:

0·1024 gave 10·5 c.c. N_2 at 33° and 763 mm. N = 11·53.

$C_{49}H_{38}O_2N_6$ requires N = 11·32 per cent.

Deep blue shades are obtained on chrome-mordanted wool with 5 per cent. of the colouring matter.

Phenyliminodinitroxanthone, $C_{13}H_6O(NO_2)_2{:}NPh$.—When α-dinitroxanthone was treated with aniline in the same way as the tetrabromo-compound a violet-blue powder was obtained which, when purified by alcoholic extraction, melted at 170—175°:

0·1195 gave 11 c.c. N_2 at 26° and 763 mm. N = 11·49.

$C_{19}H_{11}O_5N_3$ requires N = 11·44 per cent.

Pale violet shades are obtained on tannin-mordanted cotton with 5 per cent. of the colouring matter.

Azo-compounds.

β-Nitroxanthoneazo-β-naphthol, $C_{13}H_6O_2(NO_2)\cdot N_2\cdot C_{10}H_6\cdot OH$.—Half a gram of β-nitroaminoxanthone was made into a paste with 1 c.c. of concentrated hydrochloric acid, and by the addition of 20 c.c. of water a turbid solution was obtained; 0·2 gram of sodium nitrite in 5 c.c. of water was added slowly at about 0°; after some time a yellowish-white precipitate was formed. This was dissolved by adding about 20 c.c. of water, and then 0·23 gram of β-naphthol dissolved in 2 per cent. potassium hydroxide solution was added slowly; the mixture was then rendered alkaline, when a red precipitate was formed. Next day the mixture was acidified with dilute hydrochloric acid, and the precipitate collected. The product was insoluble in alcohol, moderately soluble in acetic acid, and fairly readily so in nitrobenzene or pyridine, but from none of these solvents was it obtained crystalline. The amorphous product does not melt at 300°:

0·1046 gave 10·5 c.c. N_2 at 30° and 758 mm. N = 10·36.

$C_{23}H_{13}O_5N_3$ requires N = 10·22 per cent.

It gives orange shades on chrome-mordanted wool, 5 per cent. of the colouring matter being used. The dyeing was effected by dissolving the substance in concentrated sulphuric acid, precipitating it by pouring into water, and boiling the wool with this precipitate.

β-Nitroxanthoneazo-1:5-dihydroxynaphthalene,
$C_{13}H_6O_2(NO_2)\cdot N_2\cdot C_{10}H_5(OH)_2$.

β-Nitroaminoxanthone was diazotised in a very concentrated aqueous solution in the usual way. A little more than the theoreti-

cal amount of 1:5-dihydroxynaphthalene in cold alcoholic solution was added, the combination taking place in acid solution. A dark red precipitate was formed, which after some time was collected and washed with warm alcohol to remove excess of dihydroxynaphthalene. It is moderately readily soluble in alcohol and fairly readily so in nitrobenzene. It does not melt at 300°:

0·1031 gave 8·9 c.c. N_2 at 33° and 762 mm. N = 9·71.

$C_{23}H_{13}O_6N_3$ requires N = 9·83 per cent.

Chrome-mordanted wool is dyed with 5 per cent. of the colouring matter in brown shades.

α-Nitroxanthoneazophenol, $C_{13}H_6O_2(NO_2)\cdot N_2\cdot C_6H_4\cdot OH$.—α-Nitroaminoxanthone was diazotised in the usual way and combined with phenol in alkaline solution. Next day the dark brown precipitate was collected, dried, and purified by alcoholic extraction. The substance does not melt at 300°:

0·1020 gave 10 c.c. N_2 at 31° and 760 mm. N = 11·83.

$C_{19}H_{11}O_5N_3$ requires N = 11·63 per cent.

The colouring matter dyes chrome-mordanted wool in yellowish-brown shades.

Attempts were made to prepare vat dyes in the following different ways, but without satisfactory results.

Dibromoxanthone was heated with β-diaminoxanthone in nitrobenzene solution with anhydrous cupric chloride, as well as with copper powder. The operations were repeated with dimethylaniline and with naphthalene as solvents instead of nitrobenzene. Exactly similar experiments were conducted with the β-nitroamine in the place of the β-diamino-compound. Hexabromoxanthone, which is most reactive with aniline, was also treated with both the diamino- and the nitroamino-compound.

In conclusion, the author desires to express his sincere thanks to Professor E. R. Watson for his kind encouragement and valuable suggestions.

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[*Received, October 27th*, 1915.]

LXIV.—*The Essential Oil of Cinnamomum Oliveri (Bail.) or Brisbane Sassafras.*

By George Watson Hargreaves.

Lauterer (*Proc. Roy. Soc. Queensland*, 1895, **11**, i, 22) describes *Cinnamomum Oliveri* as a handsome tree with grey, rough bark, growing in the scrubs on the North Coast Railway, Queensland. The bark contains a layer of phylloderma on the outside, and just between the cells of this, oil-ducts run along the bark.

Examination of the Oil from the Bark.

The bark was distilled in a current of steam, 71 kilos. giving about 1700 c.c. of oil, which was filtered and dried over calcium chloride. It had D^{23} 1·030 and n_D^{23} 1·5165.

Fractional Distillation of the Oil.—The oil was subjected to fractional distillation under 30 mm. pressure. It was first collected in fractions over 10°, and these refractionated, until finally the more important were collected in fractions over 1°. It was thus found that the oil (1300 grams) can be roughly divided into four main portions, namely, (1) that boiling below 90° yielding 98 grams, (2) that boiling between 90° and 120° yielding 291 grams, (3) that boiling between 120° and 135° yielding 326 grams, (4) that boiling between 135° and 155° yielding 533 grams.

Identification of Pinene, $C_{10}H_{16}$.—The fraction boiling at 77—78°/30 mm. (n_D^{27} 1·4655), which constituted roughly 12—15 per cent. of the oil, was identified as pinene by analysis (Found, C = 88·0; H = 11·8. Calc., C = 88·2; H = 11·8 per cent.), and by the preparation of the nitrosochloride melting at 108°.

Identification of d-*Camphor*, $C_{10}H_{16}O$.—From the fraction boiling between 90° and 120°/30 mm. a white solid separated during distillation, a further quantity being obtained on cooling the liquid. This was dried and distilled, when it boiled at 204°. (Found, C = 78·4; H = 10·2. Calc., C = 78·9; H = 10·5 per cent.)

The oxime was prepared and found to melt at 119°.

The white solid was therefore camphor. This substance, which was present to the amount of about 18—20 per cent. of the oil, was shown to be dextrorotatory when examined in alcoholic solution.

Identification of Safrole, $C_{10}H_{10}O_2$.—The fraction boiling between 125° and 130°/30 mm. on cooling gave a white, crystalline deposit which, when collected and fractionally crystallised, yielded a substance melting at 8°, and having D^{18} 1·09, n_D^{20} 1·535. (Found, C = 73·9; H = 6·3. Calc., C = 74·07; H = 6·17 per cent.)

The α-nitrosite melted and decomposed at 129—130°.

These experiments establish the presence of safrole to the extent of 25—27 per cent. of the oil.

Identification of Eugenyl Methyl Ether.—The fraction boiling between 140° and 150°/30 mm. on refractionation yielded a fraction boiling between 146° and 147° (under atmospheric pressure at 244°) having n_D^{27} 1·5305. (Found, C = 74·1; H = 7·6. Calc., C = 74·1; H = 7·8 per cent.)

Oxidation of this substance with potassium permanganate gave an acid melting at 179° identical with veratric acid. (Found, C = 59·1; H = 5·4. Calc., C = 59·3; H = 5·5 per cent. Silver salt. Found, Ag = 36·9. Calc., Ag = 37·4 per cent.)

The tribromo-derivative, $C_6H_{10}Br(OMe)_2 \cdot C_3H_5Br_2$, melted at 77—78°.

This compound, therefore, was clearly eugenyl methyl ether, and constituted the main fraction, being about 40—43 per cent. of the oil.

Examination of the Fraction Boiling above 150°/30 *mm.*—This fraction consisted of a dark brown oil which on redistillation gave a green oil. Since the chief product of oxidation with potassium permanganate was veratric acid, undoubtedly this fraction consisted mainly of eugenyl methyl ether and a trace of some ethereal substance, probably a decomposition product of eugenyl methyl ether.

Examination of the Oil from the Leaves.

The oil from the leaves was fractionated as described in the case of the oil from the bark.

The fractions of lower boiling point were found to contain about 25 per cent. of a mixture of two terpenes, pinene, and another terpene with a slightly higher boiling point, which gave a nitrosite. (The quantity of nitrosite obtained was too small to purify for the purpose of a melting-point determination.) This terpene was dextrorotatory, and had n_D^{20} 1·4719. It appeared in the fraction boiling between 75° and 80°/30 mm., and was probably phellandrene, but the quantity of substance available was too small for further investigation.

The pinene was again identified by means of its nitrosochloride, which in this case was found to melt and decompose at 103°, whereas that from the bark oil melted at 108°. There has been some discussion on this variation of melting point, Schimmel & Co. (*Geschäftsber.*, April, 1901) holding that it was 108°, and not 103°, as usually stated. However, the fact that decomposition takes place in one case points to the possibility of a lower melting point being registered.

The fraction next above the terpenes contained a very high percentage (approx. 60) of *d*-camphor.

The higher fractions contained at least two substances in very small quantities, one apparently being a phenol, which was obtained by extracting the fraction boiling above 150°/30 mm. with sodium hydroxide solution and ether. About 2 c.c. of this phenol were obtained. This compound, itself golden in colour, gave a green coloration with ferric chloride in alcohol:

0·1352 gave 0·3557 CO_2 and 0·1045 H_2O. C = 71·8; H = 8·6.

Consideration of these results leads one to expect a phenol of the formula $C_{10}H_{15}O_2$. A second combustion confirmed this formula.

The residue after extraction of the phenol furnished a small quantity of a green substance boiling at 263°, which gave no pronounced coloration with ferric chloride in alcohol.

Summary.

It may be seen that the oils from the bark and from the leaves of *Cinnamomum Oliveri* contain similar substances in the lower fractions, but differ in the higher ones, no safrole or eugenyl methyl ether being found in that from the leaves.

Thus the oil from the bark contains four distinct substances in approximately the following proportions:

Pinene	12—15 per cent.
d-Camphor	18—20 ,,
Safrole	25—27 ,,
Eugenyl methyl ether	40—45 ,,

The oil from the leaves contains:

Pinene, Phellandrene (?)	25 ,,
d-Camphor	60 ,,
Phenols and other substances	15 ,,

R. T. Baker (*Proc. Linn. Soc. N.S.W.*, 1897, ii, 275), in his paper on "The Cinnamomums of New South Wales, with a Special Research on the Oil of the Bark of *C. Oliveri* (Bail.)," gives somewhat incomplete results of a chemical analysis by H. G. Smith, no reference being made to the four main constituents of the oil. He suspects the presence of traces of eugenol, cinnamaldehyde, and cineole, none of which could be detected by the author of the present paper. All Smith's results, however, were based on colour reactions or odour; no analyses were carried out, nor were any derivatives prepared.

He also states that none of the terpenes of low boiling point is present, whereas the present work has shown the presence of pinene to the extent of 12—15 per cent.

Again, no mention is made by Smith of camphor, although he speaks of a stearoptene (which was not isolated) crystallising at −12°. This was probably a mixture of camphor and safrole, for the present author, using liquid ammonia as refrigerant, succeeded in fractionally crystallising these two substances, and by means of subsequent analyses and preparation of derivatives their compositions were ascertained. It is interesting to note that Margaret E. Scott (T., 1912, **101**, 1612) examined the essential oil of the leaves of another sassafras, which, however, is of a different order and species, *Athenosperma moschatum* (Australian sassafras, native of Victoria), and obtained the following results:

Eugenyl methyl ether	50—60 per cent.
Pinene	15—20 ,,
Camphor	15—20 ,,
Safrole	5—10 ,,

These four substances are identical with those found in the oil from the bark of *Cinnamomum Oliveri*, but not with those from the leaves.

The author's thanks are due to Professor B. D. Steele for kind assistance throughout the course of this research.

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[*Received, March, 7th,* 1916].

LXV.—*The Reaction of the Alkyl Nitrites with Pyridine and Quinoline.*

By CHARLES WESLEY ADDY and ALEXANDER KILLEN MACBETH.

A MIXTURE of amyl nitrite and pyridine gives a dark red liquid, from which needle-shaped crystals separate in the course of a few days. It was thought that these crystals were probably pyridine amyl nitrite or, if oxidation had occurred, pyridine amyl nitrate. They were very readily soluble in water, soluble in alcohol, and sparingly so in ether. On combustion, results were obtained that could not be reconciled with the above view.

Freshly distilled pyridine was mixed with freshly distilled amyl nitrite and sealed up in a tube. Another tube was filled with pyridine and amyl nitrate, and sealed. No crystals appeared in either, even after the lapse of several weeks. On opening the tube containing the nitrite, needles appeared in the course of a day.

These gave the nitrite reaction with acidified potassium iodide after one crystallisation from alcohol. This was apparently due to traces of amyl nitrite, as the reaction was not given after further purification. Analysis of the crystals showed them to be pyridine nitrate. (Found, N = 20·18; nitritic N = 9·70. C_5H_5N,HNO_3 requires N = 19·72; nitritic N = 9·86 per cent.)

A similar reaction takes place when quinoline is employed instead of pyridine. Analysis of these crystals shows them to be quinoline nitrate. (Found, N = 14·40; nitritic N = 7·20. C_9H_7N,HNO_3 requires N = 14·58; nitritic N = 7·29 per cent.)

α- and β-Picoline were also employed and crystals obtained, but no analyses were performed in these cases. Propyl nitrite was substituted for amyl nitrite, and the reaction proceeded as usual.

It is uncertain whether the reaction is to be expressed as a decomposition of the nitrite to alcohol and nitrous acid in the presence of moisture, and subsequent interaction at the tertiary nitrogen atom, followed by oxidation, or is the result of the removal of nitrous acid from the nitrite by the pyridine, etc., with the production of an olefine. The presence of amylene was not detected in the liquid in the case of amyl nitrite, but the latter view may be supported by the somewhat parallel case of the removal of hydrogen bromide by pyridine from, say, bromosuccinic ester. Up to the present the reaction has only been observed in the case of compounds of the pyridine type.

THE SIR DONALD CURRIE LABORATORIES,
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LXVI.—*Trimethyl- and Triethyl-sulphonium Nitrites.*

By CHARLES WESLEY ADDY and ALEXANDER KILLEN MACBETH.

IN a former paper (T., 1915, **107**, 87) dealing with the colorations produced on mixing alkyl sulphides with organic nitrites the authors had occasion to assume the existence of colourless final additive products of these substances; as these had not been isolated, such work was undertaken. The method adopted was the trituration of a sulphonium iodide with silver nitrite in the presence of a small quantity of water. Subsequent filtration gave a solution of the sulphonium nitrite containing traces of silver nitrite, the latter being removed on cooling the solution to zero after slight concen-

tration. The sulphonium nitrite was obtained by further concentration of the solution in a vacuum. *Trimethyl-* and *triethyl-sulphonium nitrites* were prepared in this way.

Trimethylsulphonium Nitrite.

Ten grams of trimethylsulphonium iodide were dissolved in about 10 c.c. of water, and the solution was triturated in a mortar with freshly prepared silver nitrite, the latter being added in small quantities until an excess was present. The liquid was separated from silver iodide and excess of silver nitrite, the precipitate being washed with a small quantity of cold water to carry away all the trimethylsulphonium nitrite. The filtrate and washings were concentrated somewhat in a vacuum over sulphuric acid, and, after being cooled to zero, filtered to remove traces of silver nitrite. After further concentration crystals of trimethylsulphonium nitrite separated in colourless, flat plates which presented a fern-like appearance when viewed under the microscope. They were extremely deliquescent, a short exposure to air causing the whole to liquefy.

The last traces of water were removable from the nitrite with some difficulty. The substance is very readily soluble in water, sparingly so in cold alcohol, and fairly readily so in hot alcohol, from which it crystallised in needles; it is almost insoluble in ether.

The percentage of nitrogen in the compound was determined by the "urea" method (I) and also by the ordinary nitrometer method (II):

(I) 0·1497 gave 27·8 c.c. N_2 at 14·5° and 761 mm. N = 11·12.
(II) 0·2180 „ 40·5 c.c. NO „ 14° „ 769 mm. N = 11·20.
$C_3H_9O_2NS$ requires N = 11·38 per cent.

On heating a small quantity of the nitrite it decomposes with a rapidity sufficient to cause a slight explosion. The substance was finally heated in a tube sealed to a U-tube immersed in a freezing mixture, and to a nitrometer in order that the products might be collected and examined.

When the apparatus was exhausted the nitrite melted and decomposed at 92—93°. The temperature of the glycerol bath was gradually raised, finally attaining 140°. A liquid collected in the U-tube which was methyl sulphide.

The gas collecting in the nitrometer consisted chiefly of nitric oxide and methyl nitrite vapour. A brown, syrupy residue remained which responded to tests for nitrates, but not for nitrites.

Triethylsulphonium Nitrite.

This was obtained by the same method as the preceding. The triethylsulphonium iodide was prepared by boiling a mixture of ethyl sulphide and ethyl iodide under reflux for three days. The product was recrystallised several times from a mixture of water and alcohol. Triethylsulphonium nitrite crystallises in flat, colourless plates which are extremely deliquescent; the last traces of water are removable with great difficulty. Its solubilities are of the same nature as in the case of the trimethyl compound. Both substances have a characteristic fishy odour:

0·2770 gave 38·4 c.c. NO at 17° and 767 mm. N = 8·25.

$C_6H_{15}O_2NS$ requires N = 8·48 per cent.

The action of heat was studied as in the preceding case. The nitrite melts and decomposes slightly at 95°, and on continuing to increase the temperature decomposition becomes more rapid. A liquid collects in the U-tube which, on fractionation, yields ethyl sulphide and ethyl nitrite. A small amount of nitric oxide is evolved. As in the former case, there is a brown, syrupy residue which responds to the tests for nitrates.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. [*Received, July 10th*, 1916.]

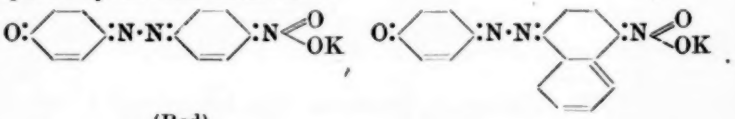
LXVII.—*The Relation Between the Chemical Constitution and Colour of Azo-compounds.*

By ANUKUL CHANDRA SIRCAR.

FROM an examination of the colour of the dyeings obtained from, and the chemical constitution of the commercial azo-dyestuffs, and also from other experiments (Sircar and Watson, *J. Soc. Chem. Ind.*, 1912, **31**, 968), it is clear that increasing the complexity of the molecule does not necessarily deepen the colour of an azo-compound, and instances are not wanting where bisazo-, trisazo-, or even tetrakisazo-dyestuffs containing one or more naphthalene nuclei and having the most complex structures give only yellow, orange, or brown dyeings. The real cause of the deepening of the colour of azo-compounds must therefore be looked for elsewhere. From an examination of their constitutional formulæ it is seen that in order that an azo-dyestuff should give dyeings of a deeper

shade than orange or brown * the auxochrome should be contained, not in a benzene, but in a naphthalene nucleus. It is further found that with a given complexity of the molecule the relative positions of the auxochromic and chromophoric groups have an obvious effect on the colour of an azo-compound, the ortho-position favouring red, violet, and blue shades, and the para-position giving orange or brown shades. Thus one arrives at the conclusion that to deepen the colour of an azo-compound the first condition to be satisfied is to have the auxochrome in a naphthalene nucleus, preferably in the ortho-position with respect to the azo-linking.

Hewitt and Mitchell (T., 1906, **89**, 18) showed that all *p*-nitrohydroxyazo-compounds exhibit remarkable changes of colour when dissolved in alkali, and suggested that in such cases no simple salt-formation, but transformation of the nitroazo-structure into the *iso*nitro-*iso*azo-form (with a diquinonoid structure) takes place. In a subsequent paper (T., 1907, **91**, 1251) these authors drew the conclusion that in an azo-compound the chief oscillation frequency is less, that is, the colour is deeper the longer the chain of alternative double and single linkings in the molecule, and explained the difference in the colour of the alkaline solutions of *p*-nitrobenzeneazophenol and *p*-nitrobenzene-1-azo-4-naphthol as due to the potassium salt of the former containing a chain in which there are 6 double and 5 single bonds placed alternately, and that of the latter a similar chain of 8 double and 7 single bonds respectively in their molecules:



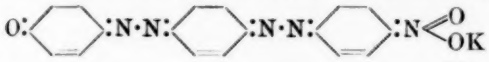
(Red).

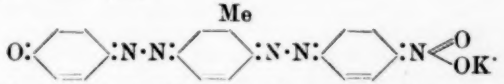
In view of these observations, it seemed interesting to examine whether *p*-nitrohydroxyazo-compounds containing the auxochrome in the benzene nucleus and a long chain of alternate double and single linkings in their molecules will exhibit the same changes of colour as are shown by *p*-nitrobenzene-1-azo-4-naphthol and *p*-nitrobenzene-1-azo-4-naphthol-3-carboxylic acid when dissolved in alkali.

p-Nitrobenzeneazobenzeneazophenol (Pope and Willett, T., 1913, **103**, 1258) dissolves in alkali with a purple colour, and *p*-nitrobenzeneazo-*m*-xyleneazophenol (Meldola, T., 1883, **43**, 430) does so with a reddish-violet colour. These facts, instead of supporting (compare Pope and Willett, *loc. cit.*), seem rather to militate against Hewitt and Mitchell's theory, for, according to these

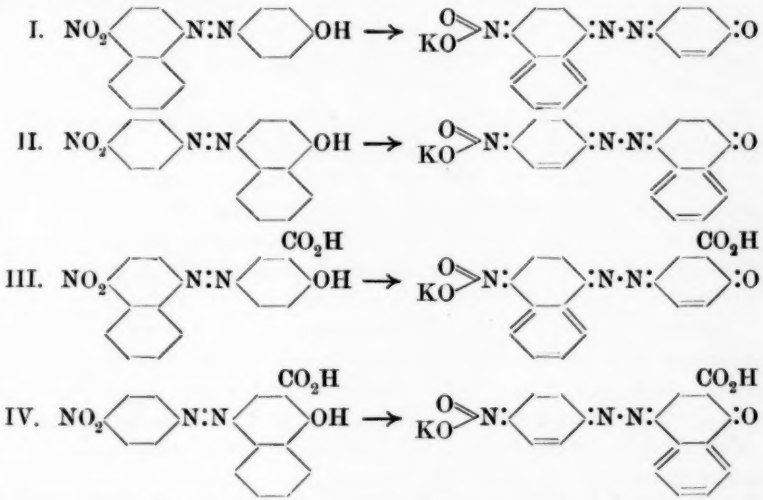
* The colours are arranged in the following order:—yellow, orange, scarlet, crimson, violet, blue, and green, and the colour is said to deepen as it passes from one on the left- to one on the right-hand side of the order.

authors, as the following potassium salts contain chains with alternately 9 double and 8 single bonds in their molecules, they should dissolve in alkali with a blue or even a deeper colour.





In order to test the point further, 4-nitronaphthalene-1-azophenol and 4-nitronaphthalene-1-azosalicylic acid have been prepared. These two compounds are isomeric with, and should possess exactly similar diquinonoid arrangements in alkali as, *p*-nitrobenzene-1-azo-4-naphthol and *p*-nitrobenzene-1-azo-4-naphthol-3-carboxylic acid:



Comparing I and II, it is seen that in alkaline solutions they contain the same number of alternate double and single bonds in their molecules, and therefore they should dissolve in alkali with the same (blue) colour and produce absorption spectra similar and alike in nature.

The two *p*-nitronaphthalene-1-azophenolic compounds are found to dissolve in alkali only with a red colour. This fact and the nature of the absorption spectra produced by these two compounds are directly in opposition to Hewitt and Mitchell's conclusions (T., 1907, **91**, 1251). It may be mentioned here that Baly, Tuck, and Marsden (T., 1910, **97**, 1494) have shown that alkali salts of *p*-nitro-*p*-hydroxyazo-compounds are not quinoneazines as supposed by Hewitt and Mitchell.

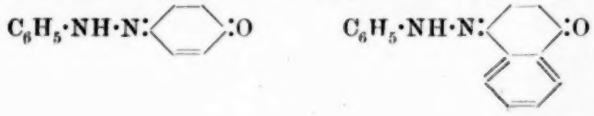
The colour of the alkaline solutions and the dyeings obtained on wool of the various *p*-nitroazo-compounds just discussed are compared below:

p-Nitroazo-compound.	Colour of the alkaline solution.	Colour of the dyeings on wool with 2 per cent. dye-stuff.
p-Nitrobenzeneazophenol...	Red	Orange-yellow.
4-Nitronaphthalene-1-azophenol	Deep-red	,,
p-Nitrobenzene-1-azo-4-naphthol	Blue	Orange-red.
p-Nitrobenzeneazosalicyclic acid	Red	Orange-yellow.
4-Nitronaphthalene-1-azo-salicylic acid ...	Deep-red	,,
p-Nitrobenzene-1-azo-4-naphthol-3-carboxylic acid	Blue	Brownish-red.
p-Nitrobenzeneazobenzeneazophenol	Purple	Rich brown.
p-Nitrobenzeneazo-*m*-xyleneazophenol ...	Reddish-violet	Orange-brown.

It is found that the azonaphthols give red dyeings, whilst the azophenols give yellow or orange dyeings. Such a difference in the colour of the dyeings obtained from the isomeric pairs of substances is quite in agreement with the view already expressed, namely, that to deepen the colour of an azo-compound the first condition to be satisfied is to have the auxochrome in a naphthalene and not in a benzene nucleus.

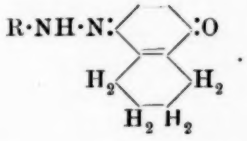
Now, naturally the question arises why, in order to produce an azo-dyestuff giving deeper colour than orange or brown, the auxochrome should necessarily be contained in the naphthalene nucleus. The argument that the deepening of colour in such cases is due to the auxochrome being contained in a complex nucleus is scarcely tenable. Many dyestuffs are known in which the auxochromes are contained in nuclei more complex than naphthalene, but which scarcely give dyeings of deeper colour than red. Again, any difference in the structure of the molecules of the azophenols and the azonaphthols as the cause of the difference in their colours cannot be accepted.

On examining the molecular structures of phenol and naphthol, it is found that the molecule of the latter, as compared with the molecule of the former, contains a larger number of alternate double and single bonds, and it is found (see below) that in an azo-compound the longer the chain of alternate double and single bonds in the part of the molecule containing the auxochrome, proceeding from the auxochrome up to the azo-linking, taking the longest possible route, the deeper is the colour. Comparing the formulæ of benzeneazophenol and benzeneazo-α-naphthol,



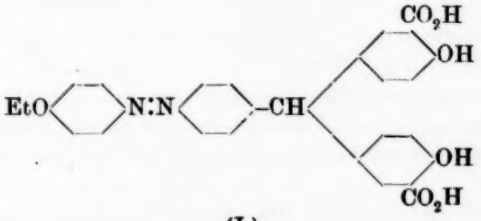
it is seen that the chain in the former consists of alternating 3 double and 2 single bonds, whereas in the latter case it consists alternately of 5 double and 4 single bonds. The former gives yellow and the latter orange-red dyeings on wool. In counting such alternate double and single bonds, one should not go beyond the azo-linking, as proposed by Hewitt and Mitchell in the case of *p*-nitroazo-compounds (T., 1907, **91**, 1257).

In order to test the validity of the conclusion, benzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol, *p*-nitrobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol, *p*-bromobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol, and *p*-sulphobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol have been prepared and examined. These compounds contain the auxochromes in the naphthalene nuclei, but the length of the desired chain in them is shorter and consists of only 3 double and 2 single bonds:

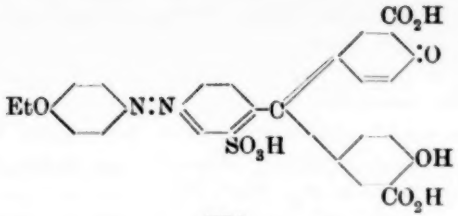


They are in this respect comparable with the azophenols. These azotetrahydronaphthols are all yellow, and give dyeings almost identical in colour with those given by the corresponding azophenols.

The difference in the lengths of the chain of alternate double and single bonds in the nuclei containing the auxochrome being the primary cause of the difference of colour of any two azo-compounds, it cannot be maintained that in order to produce azodyestuffs giving deeper colours than orange or brown the auxochrome should necessarily be contained in a naphthalene nucleus. The naphthalene nucleus is only advantageous in providing such a long chain. Green and Sen (T., 1912, **101**, 1171) prepared phenetoleazosulphophenyldihydroxydiphenylmethanedicarboxylic acid (I):



(I.)

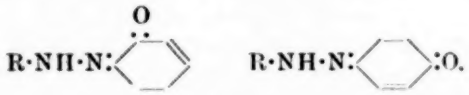


(II.)

It dyes wool yellow, but its oxidation product (II) dyes wool red. The cause of the deepening of colour in the latter case is evident when it is considered that it contains a chain of 6 double and 5 single bonds placed alternately, but that in the former such a chain is not conceivable.

The reason why the azo-derivative obtained by using such complexes as 2:2′-dihydroxydiphenyl (Robertson and Brady, T., 1913, **103**, 1484), catechin (A. G. Perkin and Yositake, T., 1902, **81**, 1160), substituted pyrazoles (Bülow and Hecking, *Ber.*, 1911, **44**, 467), and phenyl*iso*oxazolone (Meyer, *Compt. rend.*, 1913, **156**, 1992) as end components do not give dyeings of deeper colours than orange or brown is now obvious. In none of these cases is the length of the required chain in the nucleus containing the auxochrome very great, it being naturally short or broken.

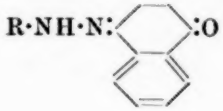
As a further test of the theory, the preparation of azoanthrols suggested itself. Some azo-derivatives of β-anthrol are known (Liebermann, D.R.-P., 21178 of 1882), but in these compounds the auxochromic and chromophoric groups are in the ortho-position with respect to each other, and, as has been said before, such relative positions favour the formation of deep colours. It may be argued that deeper colours are obtained when the auxochromic and chromophoric groups are in the ortho-position, and comparatively lighter colours when they are in the para-position with respect to each other, because in the former case there is a comparatively longer chain of alternate double and single bonds running from the auxochrome to the chromophore, thus:



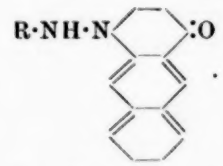
It is, however, premature to draw any such conclusions before further experimental work has been done on the subject, and only *p*-hydroxyazo-compounds have been chosen for the present investigation.

Lagodinski (*Ber.*, 1906, **39**, 1717) has shown that α-anthrol combines with diazonium salts to form bluish-red azo-compounds,

but he did not isolate any of them. Benzene-1-azo-4-anthrol, *p*-nitrobenzene-1-azo-4-anthrol, *p*-bromobenzene-1-azo-4-anthrol, and *p*-sulphobenzene-1-azo-4-anthrol have now been prepared and examined. They dye wool in reddish-violet shades, whereas the corresponding azo-**α**-naphthols dye wool only in orange or reddish-orange shades. This is quite in agreement with the view already expressed, for the chain in the case of the azo-**α**-naphthols consists alternately of 5 double and 4 single bonds, and in the case of the azo-**α**-anthrols of 7 double and 6 single bonds alternately:



As a still further test of the theory, the dyeing properties of benzeneazoanthranol and *p*-nitrobenzeneazoanthranol (Kaufler and Suchaunell, *Ber.*, 1907, **40**, 518) have been examined. That in these compounds the azo-linking occupies the para-position with respect to the hydroxyl group is evident from the preparation of benzeneazoanthranol by the condensation of 9:9′-dibromoanthrone with alcoholic phenylhydrazine (Meyer and Zahn, *Annalen*, 1913, **396**, 152). These compounds are isomeric with, and have the same molecular complexity as, the corresponding azo-**α**-anthrols. It will be seen from their formulæ that although the total number of alternate double and single bonds in the molecules of the azo-**α**-anthrols and azoanthranols are equal,

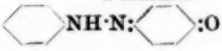
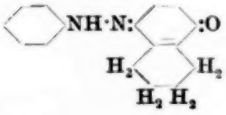
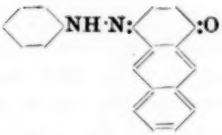
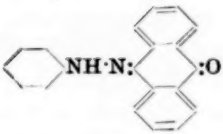
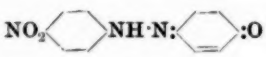
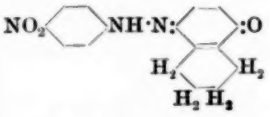
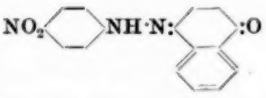


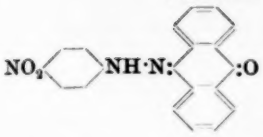
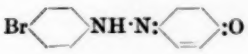
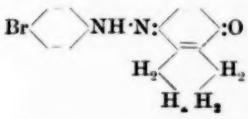
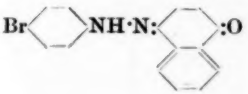
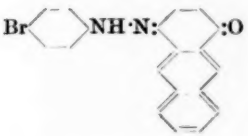
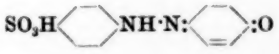
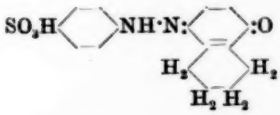
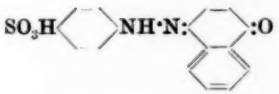
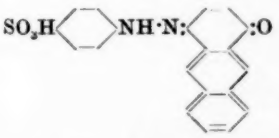
in the case of the azoanthranols the chain of alternate double and single bonds, proceeding one way or the other, from the auxochrome to the chromophore consists of only 5 double and 4 single bonds, that is, is equal to that in the azo-**α**-naphthols. The dyeings with the azoanthranols should therefore be lighter in colour than those obtained with the azo-**α**-anthrols. In fact, the azoanthranols dye wool in yellow shades.

On account of the very sparing solubility of the azo-**α**-anthrols and azoanthranols in water, they were first dissolved in sulphuric

acid, precipitated by water, collected, and the precipitate washed until free from acids, and afterwards used for dyeing. Full shades were, however, not obtained, as much of the colouring matter was left in the dye-bath.

A comparison of the colour of the dyeings obtained on wool with the various azotetrahydronaphthols, azo-α-anthrols, azo-anthranols, and the corresponding azophenols and azo-α-naphthols is made below:

Formula.	M. p.	Colour of the dyeing obtained on wool with 2 per cent. dye-stuff.
	157°	Yellow.
	146°	Yellow.
	206°	Orange.
	—	Reddish-violet.
	—	Yellow.
	212—213°	Yellow.
	205—217°	Yellow.
	277—279°	Orange-red.
	—	Reddish-violet.

Formula.	M. p.	Colour of the dyeing obtained on wool with 2 per cent. dye-stuff.
	—	Yellow.
	155°	Yellow.
	147—148·5°	Yellow.
	237—238°	Reddish-orange.
	—	Reddish-violet.
	—	Yellow.
	—	Yellow.
	—	Fiery-orange.
	—	Reddish-violet.

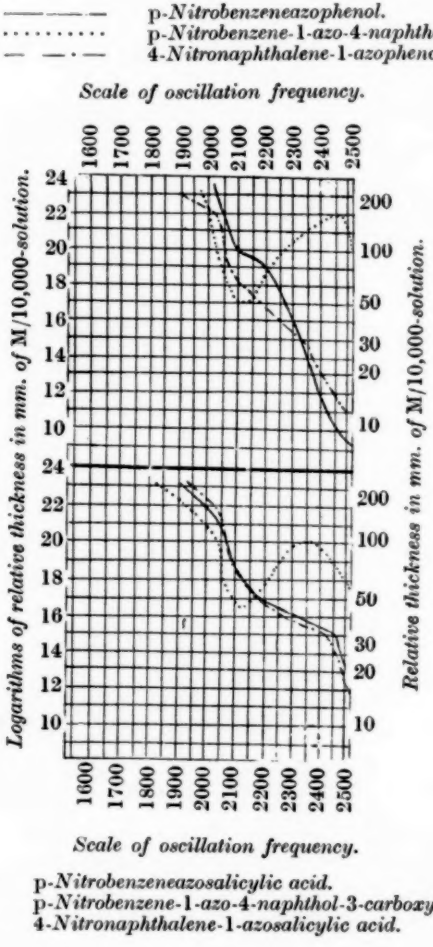
It is seen from the table that in an azo-compound the longer the chain of alternate double and single bonds in the part of the molecule containing the auxochrome, going from the auxochrome to the azo-linking, taking the longest possible route, the deeper is the colour, and vice versâ.

An examination of the absorption spectra (Figs. 3, 4, 5, and 6) also reveals the fact that in an azo-compound as the length of

the chain referred to before is increased, so is the head of the absorption band gradually shifted towards the red end of the spectrum, and vice versâ.

On the other hand, the absorption curves of the potassium salts

FIG. 1.


p-Nitrobenzeneazophenol.
p-Nitrobenzene-1-azo-4-naphthol.
4-Nitronaphthalene-1-azophenol.
Scale of oscillation frequency.
1600 1700 1800 1900 2000 2100 2200 2300 2400 2500
Logarithms of relative thickness in mm. of M/10,000-solution.
Relative thickness in mm. of M/10,000-solution.
24 22 20 18 16 14 12 10
200 100 50 30 20 10
Scale of oscillation frequency.
p-Nitrobenzeneazosalicylic acid.
p-Nitrobenzene-1-azo-4-naphthol-3-carboxylic acid.
4-Nitronaphthalene-1-azosalicylic acid.

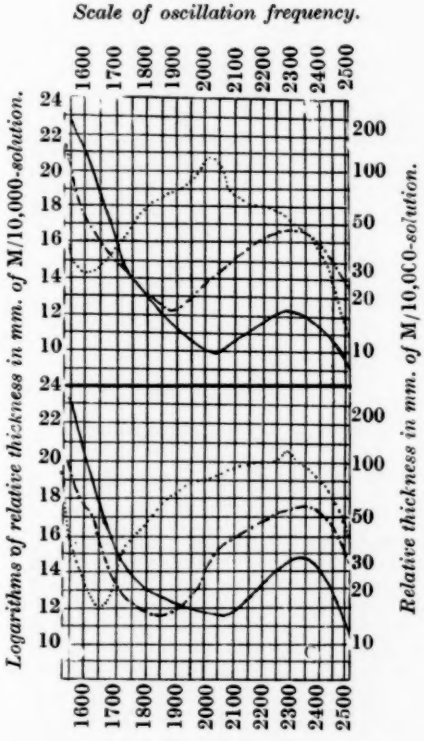
of azotetrahydronaphthols and azoanthranols (Figs. 7, 8, 9, and 10) are found to be much like the absorption curves of the potassium salts of the corresponding azo-α-naphthols and azo-α-anthrols respectively. These facts seem fully to support the view expressed by Hantzsch (*Ber.*, 1899, **32**, 3089), that the salts of

p-hydroxyazo-compounds are true derivatives of hydroxyazobenzene.

The absorption spectra produced by the azo-dyestuffs under examination in the visible part of the spectrum only have been

FIG. 2.

——— p-*Nitrobenzeneazophenol* (*potassium salt*).
..... p-*Nitrobenzene*-1-*azo*-4-*naphthol* (*potassium salt*).
—·—·— 4-*Nitronaphthalene*-1-*azophenol* (*potassium salt*).

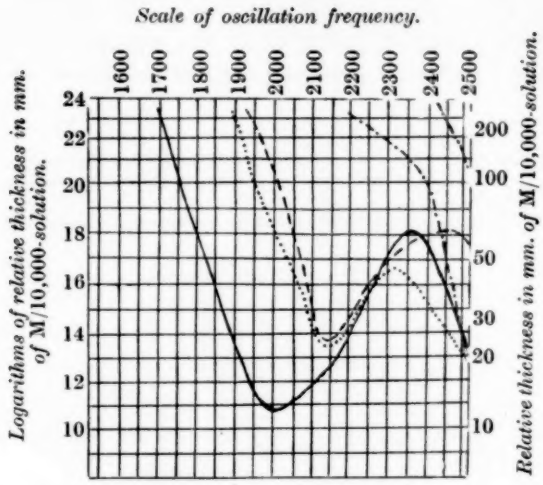

Scale of oscillation frequency.
1600 1700 1800 1900 2000 2100 2200 2300 2400 2500
Logarithms of relative thickness in mm. of M/10,000-solution.
24 22 20 18 16 14 12 10
Relative thickness in mm. of M/10,000-solution.
200 100 50 30 20 10
Scale of oscillation frequency.

——— p-*Nitrobenzeneazosalicylic acid* (*potassium salt*).
..... p-*Nitrobenzene*-1-*azo*-4-*naphthol*-3-*carboxylic acid* (*potassium salt*).
—·—·— 4-*Nitronaphthalene*-1-*azosalicylic acid* (*potassium salt*).

considered, as in judging the colour of a dyestuff we are concerned only with the absorption produced by it in the visible part of the spectrum.

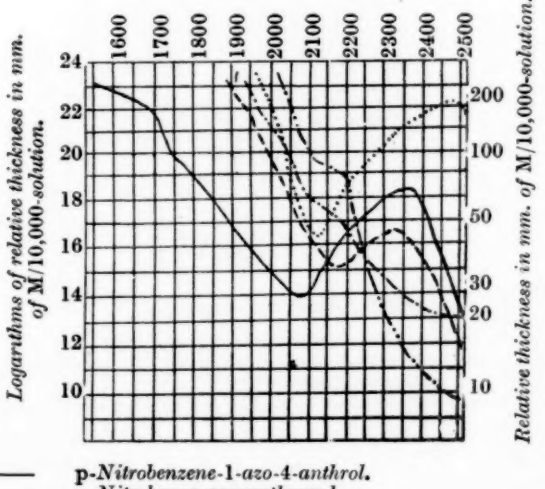
All the solutions examined were alcoholic, the solutions of the

FIG. 3.



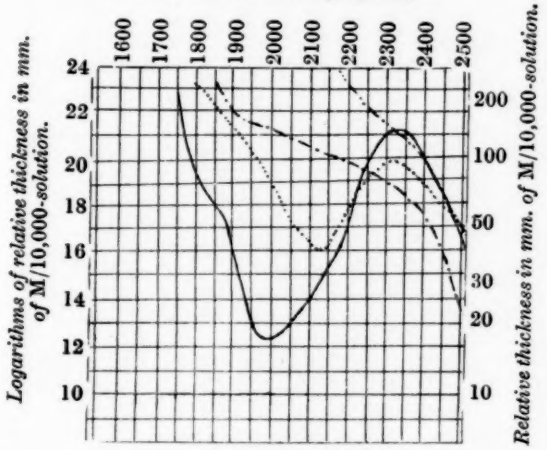
——— *Benzene-1-azo-4-anthrol.*
– – – – *Benzeneazoanthranol.*
..... *Benzene-1-azo-4-naphthol.*
—·—·— *Benzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol.*
—··—·· *Benzeneazophenol.*

FIG. 4.



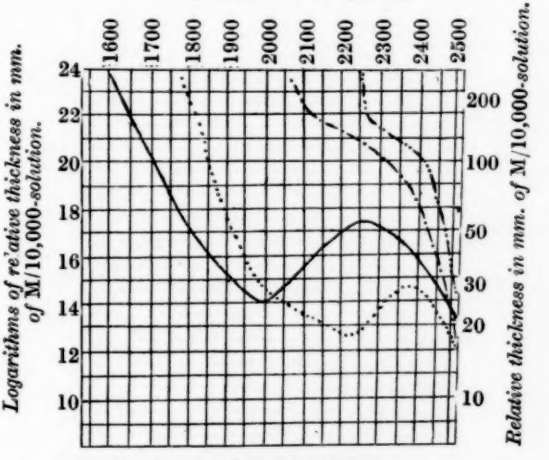
——— p-*Nitrobenzene-1-azo-4-anthrol.*
– – – – p-*Nitrobenzeneazoanthranol.*
..... p-*Nitrobenzene-1-azo-4-naphthol.*
—·—·— p-*Nitrobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol.*
—··—·· p-*Nitrobenzeneazophenol.*

FIG. 5.



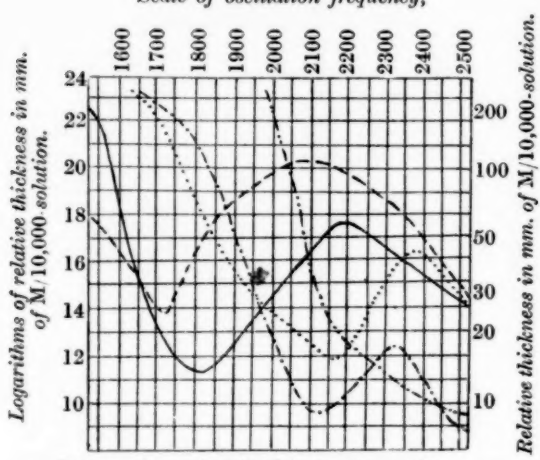
——— p-*Bromobenzene-1-azo-4-anthrol.*
····· p-*Bromobenzene-1-azo-4-naphthol.*
— · — · — p-*Bromobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol.*
— · · — · · p-*Bromobenzeneazophenol.*

FIG. 6.



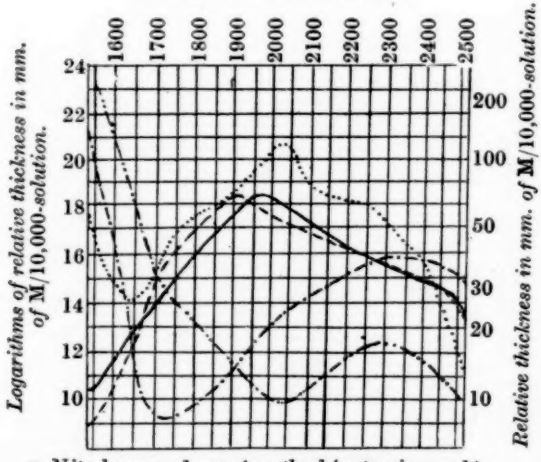
——— p-*Sulphobenzene-1-azo-4-anthrol.*
····· p-*Sulphobenzene-1-azo-4-naphthol.*
— · — · — p-*Sulphobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol.*
— · · — · · p-*Sulphobenzeneazophenol.*

FIG. 7.



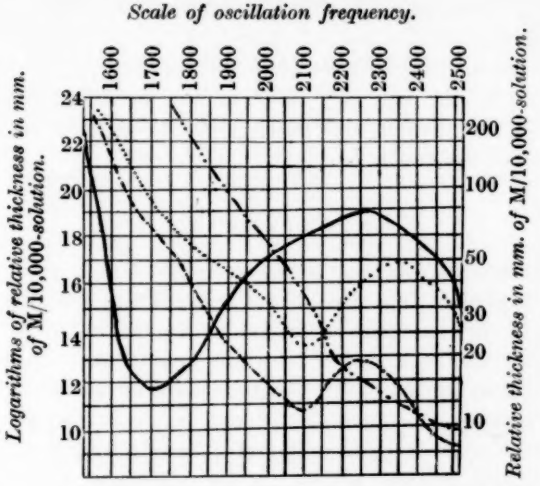
——— ——— *Benzene-1-azo-4-anthrol (potassium salt).*
– – – – – *Benzeneazoanthranol (potassium salt).*
. . . . . *Benzene-1-azo-4-naphthol (potassium salt).*
— · — · — *Benzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol (potassium salt).*
— · · — · · *Benzeneazophenol (potassium salt).*

FIG. 8.



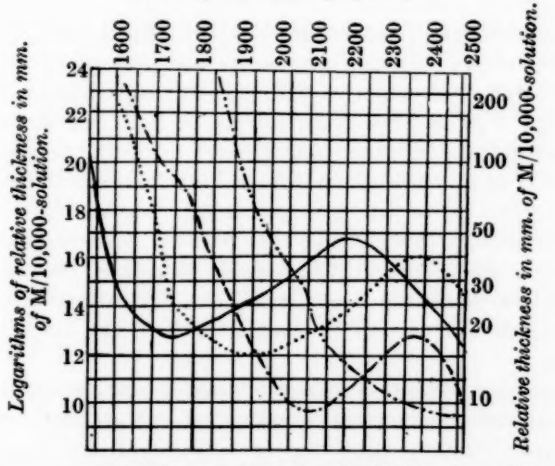
——— ——— p-*Nitrobenzene-1-azo-4-anthrol (potassium salt).*
– – – – – p-*Nitrobenzeneazoanthranol (potassium salt).*
. . . . . p-*Nitrobenzene-1-azo-4-naphthol (potassium salt).*
— · — · — p-*Nitrobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol (potassium salt).*
— · · — · · p-*Nitrobenzeneazophenol (potassium salt).*

FIG. 9.



——— p-*Bromobenzene-1-azo-4-anthrol* (*potassium salt*).
..... p-*Bromobenzene-1-azo-4-naphthol* (*potassium salt*).
— · — · — p-*Bromobenzene-1-azo-1′ : 2′ : 3′ : 4-tetrahydro-4-naphthol* (*potassium salt*).
— · · — · · p-*Bromobenzeneazophenol* (*potassium salt*).

FIG. 10.



——— p-*Sulphobenzene-1-azo-4-anthrol* (*potassium salt*).
..... p-*Sulphobenzene-1-azo-4-naphthol* (*potassium salt*).
— · — · — p-*Sulphobenzene-1-azo-1′ : 2′ : 3′ : 4′-tetrahydro-4-naphthol* (*potassium salt*).
— · · — · · p-*Sulphobenzeneazophenol* (*potassium salt*).

potassium salts being prepared by adding three or four drops of 50 per cent. potassium hydroxide solution to 100 c.c. of the alcoholic solution of the parent substance.

It is also interesting to note that the melting points of the azo-tetrahydronaphthols are very near to the melting points of the corresponding azophenols and much lower than those of the corresponding azo-α-naphthols.

Experimental.

4-Nitro-α-naphthylamine.—Aceto-α-naphthalide was nitrated (Lillmann and Remfry, *Ber.*, 1886, **19**, 797), and by selective hydrolysis of the product a mixture, containing two forms of crystals fairly distinguishable by their colour and appearance, of 4-nitro-α-naphthylamine and 2-nitroaceto α-naphthalide was obtained. The two substances could not be separated by following the original directions (*loc. cit.*), but it was found that on adding to the mixture sodium nitrite in the presence of concentrated hydrochloric acid, 4-nitro-α-naphthylamine was diazotised and passed into solution, leaving the 2-nitroaceto-α-naphthalide in suspension. The latter substance was separated by filtration, washed, crystallised from alcohol, and identified. A blank experiment showed that the mixture contained 50 per cent. of 4-nitro-α-naphthylamine, and in preparing the two azo-compounds described below appropriate quantities of the second components were employed.

4-Nitronaphthalene-1-azophenol, $NO_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_4 \cdot OH$.—Two grams of the above mixture were made into fine paste with 15 c.c. of concentrated hydrochloric acid, cooled, and diazotised with a solution of 0·5 gram of sodium nitrite in 2 c.c. of water. After twenty minutes the mixture was filtered, and the solution added slowly to a cold alkaline solution of 0·7 gram of phenol in 250 c.c. of water, when a brown precipitate of the azo-compound was formed. Next day the mixture was warmed with excess of hydrochloric acid, when the dirty-brown precipitate became orange-brown. After collecting and drying, it crystallised from dilute alcohol in pale red needles melting at 182—183°, the yield being 1·2 grams.

The compound is soluble in alcohol, acetic acid, acetone, benzene, or nitrobenzene, moderately so in ether, chloroform, or methyl alcohol, and insoluble in water or cold alkali hydroxide. In a boiling solution of alkali hydroxide it dissolves with a deep red, and in concentrated sulphuric acid with a magenta colour. It dyes wool bright yellow:

0·1241 gave 16 c.c. N_2 (moist) at 30° and 760·9 mm. N = 14·32.
$C_{16}H_{11}O_2N_3$ requires N = 14·30 per cent.

4-Nitronaphthalene-1-azosalicylic acid,
$NO_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H$.
—A diazotised solution of 4-nitro-α-naphthylamine was added to an alkaline solution of slightly more than the theoretical quantity of salicylic acid, and the product worked up as before. A brownish-yellow precipitate was obtained, which crystallised from nitrobenzene in yellowish-red needles softening at 199—200° and melting at 222—223°. It is fairly readily soluble in methyl and ethyl alcohols, benzene, acetone, chloroform, ether, acetic acid, or nitrobenzene, but insoluble in water or cold dilute alkali hydroxide. It dissolves in boiling alkali hydroxide solution with a deep red, and in concentrated sulphuric acid with a violet colour. It dyes both unmordanted and chrome-mordanted wool orange-yellow:

0·1295 gave 14·4 c.c. N_2 (moist) at 26° and 763·2 mm. N = 12·61.
$C_{17}H_{11}O_5N_3$ requires N = 12·46 per cent.

p-Sulphobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol.—Bamberger and Bordt (*Ber.*, 1890, **23**, 217) prepared the sodium salt of this compound, but not the free acid.

A diazotised solution of 0·865 gram of sulphanilic acid was added to 0·74 gram of 1′:2′:3′:4′-tetrahydro-α-naphthol dissolved in excess of sodium hydroxide. After a few minutes the whole was exactly neutralised with glacial acetic acid, when an orange precipitate of the sodium salt was produced, which was collected, dried, and crystallised from boiling water, separating in bronzy plates (1 gram).

To the filtrate concentrated hydrochloric acid was added drop by drop, when a turbidity appeared. The addition of acid was stopped when the turbidity was at its maximum, and, after two hours, the orange needles of the free acid were collected and dried (0·5 gram).

The compound dissolves in methyl and ethyl alcohols, acetone, acetic acid, or water, but is almost insoluble in light petroleum, benzene, or chloroform. It dissolves in alkali hydroxide with an orange-red, and in concentrated sulphuric acid with a red colour. It dyes in full yellow shades:

0·1029 gave 8 c.c. N_2 (moist) at 24° and 752 mm. N = 8·73.
$C_{16}H_{16}O_4N_2S$ requires N = 8·47 per cent.

p-Nitrobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol.—A diazotised solution of 0·69 gram of *p*-nitroaniline was combined as in the last experiment with an alkaline solution of 0·74 gram of

1′:2′:3′:4′-tetrahydro-α-naphthol. After a few minutes the precipitate formed was treated with concentrated hydrochloric acid, and the orange-coloured flocks obtained in this way were collected and dried on a porous plate. Amyl alcohol was the only solvent from which the substance could be crystallised; it separated in aggregates of orange prisms, softening at about 205° and melting at 217°. It is soluble in methyl, ethyl, or amyl alcohols, nitrobenzene, benzene, toluene, acetone, chloroform, or acetic acid, but is insoluble in light petroleum or water. It dissolves in alkali hydroxide solution with an orange-red, and in concentrated sulphuric acid with a red colour, and dyes wool in full yellow shades:

0·1210 gave 15 c.c. N_2 (moist) at 23° and 762 mm. N = 14·0.
$C_{16}H_{15}O_3N_4$ requires N = 14·14 per cent.

p-*Bromobenzene*-1-*azo*-1′:2′:3′:4′-*tetrahydro*-4-*naphthol*.—A diazotised solution of 0·86 gram of *p*-bromoaniline was combined with 0·74 gram of 1′:2′:3′:4′-tetrahydro-α-naphthol in alkaline solution. After thirty minutes the mixture was acidified, and the brown precipitate collected and dried. It crystallises from alcohol with the addition of a few drops of water in orange-yellow needles melting at 147—148·5° (yield 1·3 grams). It is soluble in acetic acid, benzene, chloroform, acetone, or ether, but almost insoluble in light petroleum or water. It dissolves in alkali hydroxide solution with an orange-red, and in concentrated sulphuric acid with a red colour. It dyes wool yellow:

0·1400 gave 10·6 c.c. N_2 (moist) at 27° and 760·2 mm. N = 8·66.
$C_{16}H_{15}ON_2Br$ requires N = 8·48 per cent.

Anthracene-α-monosulphonic Acid.—Anthraquinone was sulphonated as directed by Schmidt (*Ber.*, 1904, **37**, 67), but the best yield was obtained by using fuming sulphuric acid containing 25—30 per cent. of sulphur trioxide. The reduction of the potassium salt of anthraquinone-α-monosulphonic acid thus formed by zinc dust and ammonia required only twenty-five to thirty minutes (compare Schmidt, *ibid.*, p. 70). As the yield of the crystals appearing on cooling was rather poor, the whole of the clear, filtered solution was evaporated to dryness, and the potassium anthracene-α-monosulphonate utilised for the next operation.

α-*Anthrol* (Dienel, *Ber.*, 1905, **38**, 2868; Schmidt, *Ber.*, 1904, **37**, 70).—Two grams of potassium anthracene-α-monosulphonate were fused with 10 grams of potassium hydroxide at 250—260°, the fusion being kept at that temperature for twenty-five minutes,

and afterwards allowed to cool. Four or 5 c.c. of water, and then 6—7 c.c. of concentrated hydrochloric acid, were added, and the whole was poured into about 100 c.c. of water, when a brown precipitate separated. This crystallised in yellowish-white, shining plates, melting at 152° (1 gram), by dissolving in the smallest quantity of boiling acetic acid, and then shaking with about thrice its volume of water. It was further purified by a second crystallisation from dilute alcohol.

Benzene-1-*azo*-4-*anthrol*.—A diazotised solution of 0·2 gram of aniline was added to a solution of 0·4 gram of α-anthrol in 6 c.c. of alcohol. After some time a precipitate separated from the deep red solution; this was collected next day and dissolved in an excess of 25 per cent. aqueous potassium hydroxide, forming a magenta-violet solution. The solution was next acidified with concentrated hydrochloric acid, when the free azo-compound separated. After being collected and dried, it crystallised from benzene in violet-red, shining needles melting and decomposing at 234—235°. The substance is soluble in methyl or ethyl alcohols, acetone, chloroform, benzene, toluene, xylene, acetic acid, nitrobenzene, or ether, but insoluble in water, light petroleum, or aqueous potassium hydroxide. It dissolves in concentrated sulphuric acid to a violet-black solution, and in alcoholic potassium hydroxide with a reddish-violet colour. It dyes wool reddish-violet:

0·1076 gave 9·2 c.c. N_2 (moist) at 30° and 759 mm. N = 9·26.
$C_{20}H_{14}ON_2$ requires N = 9·39 per cent.

p-*Bromobenzene*-1-*azo*-4-*anthrol*.—A diazotised solution of 0·355 gram of *p*-bromoaniline was combined, as in the last experiment, with 0·4 gram of α-anthrol dissolved in 10 c.c. of alcohol. On repeated crystallisation from xylene it separated in dark, reddish-violet, microscopic needles melting and decomposing at 248—249°. The compound is soluble in methyl or ethyl alcohols, acetic acid, acetone, benzene, toluene, xylene, chloroform, nitrobenzene, or amyl alcohol, but insoluble in water or aqueous alkali hydroxide; it dissolves in concentrated sulphuric acid to a blue-black solution, and in alcoholic potassium hydroxide with a violet colour. It dyes wool reddish-violet:

0·1226 gave 8·5 c.c. N_2 (moist) at 27° and 764·5 mm. N = 7·80.
$C_{20}H_{13}ON_2Br$ requires N = 7·45 per cent.

p-*Nitrobenzene*-1-*azo*-4-*anthrol*.—A diazotised solution of 0·214 gram of *p*-nitroaniline was added to an alcoholic solution of 0·3 gram of α-anthrol. Next day the red precipitate was collected

and treated with dilute aqueous potassium hydroxide, when it turned black. The precipitate was collected, treated with concentrated hydrochloric acid, warmed, again collected, and dried. For purification it was dissolved in nitrobenzene and precipitated with light petroleum. It forms a dark red powder melting at above 285°. It is soluble in acetone, chloroform, or nitrobenzene, moderately so in ethyl or methyl alcohols, acetic acid, benzene, or ether, and dissolves in concentrated sulphuric acid to a blue-black solution and in alcoholic potassium hydroxide with a greenish-blue colour. It dyes wool reddish-violet:

0·1302 gave 13·4 c.c. N_2 (moist) at 22° and 764 mm. N = 11·88.

$C_{20}H_{13}O_3N_3$ requires N = 12·24 per cent.

p-*Sulphobenzene*-1-*azo*-4-*anthrol*.—A diazotised solution of 0·447 gram of sulphanilic acid was combined with a solution of 0·5 gram of α-anthrol in excess of alkali hydroxide. On acidifying the solution next day, a purple-coloured precipitate separated, but it could not be crystallised. The compound forms a dark red powder, which is moderately soluble in alcohol, nitrobenzene, or water, insoluble in benzene, light petroleum, or ether, and soluble in concentrated sulphuric acid with a blue-black, and in alcoholic potassium hydroxide with a violet colour. It dyes wool bright violet:

0·1116 gave 7 c.c. N_2 (moist) at 25° and 761·5 mm. N = 7·12.

$C_{20}H_{14}O_4N_2S$ requires N = 7·40 per cent.

In conclusion, I beg to express my best thanks to Dr. E. R. Watson for the kind help and encouragement which he has given me during the course of this investigation.

CHEMICAL LABORATORY, DACCA COLLEGE,
DACCA, E. BENGAL, INDIA. [*Received, October 13th*, 1915.]

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

WHINFIELD,
SALCOMBE,
S. DEVON,
July 27th, 1916.

GENTLEMEN,

I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1917.

Comparatively few determinations of atomic weights have been published since the last Annual Report, and those that have appeared would seem to necessitate no immediate alteration in the table submitted this time last year, with the single exception of the value previously assigned to Columbium. It is now suggested that Cb should be altered to 93·1. Otherwise the table for 1916 may be reprinted as it stands.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
London.

Annual Report of the International Committee on Atomic Weights, 1917.

The following new determinations of Atomic Weights have been published since the issue of the last Annual Report:

Hydrogen.—Burt and Edgar (*Phil. Trans.*, 1916, **216**, 393) conclude from a long series of experiments that the ratio of the combining volumes of Hydrogen and Oxygen is represented with a high degree of probability by the figure 2·00288 at 0° and 760 mm. pressure. Assuming Morley's values for the densities of hydrogen and oxygen, namely, 0·089873 and 1·42900 respectively, the atomic weight of hydrogen is found to be 1·00772. This new value for H is very nearly the arithmetic mean of the independent values obtained by Morley and Noyes. It may be taken, therefore, that the true value for H lies very close to 1·0077.

Zinc.—Baxter and Grose (*J. Amer. Chem. Soc.*, 1916, **38**, 868), by the electrolysis of zinc bromide, find Zn = 65·388.

Cadmium.—Baxter, Grose, and Hartmann (*J. Amer. Chem. Soc.*, 1916, **38**, 857), by the electrolysis of cadmium bromide, find Cd = 112·407. Similar analyses of the chloride gave Cd = 112·413. Œchsner de Coninck and Gérard (*Compt. rend.*, 1915, **161**, 676), by reducing cadmium carbonate to metal, found Cd = 112·32.

Lead.—Höningschmid and Horovitz (*Monatsh.*, 1915, **36**, 355), by analyses of the chloride, found for common lead the value Pb = 207·180. Similar analyses of radioactive lead chloride from various sources gave atomic weight values ranging from 206·050 to 206·084.

Bismuth.—Œchsner de Coninck and Gérard (*Compt. rend.*, 1916, **162**, 252), by reduction of bismuth chloride to metal, found Bi = 208·50.

Molybdenum.—Müller (*J. Amer. Chem. Soc.*, 1915, **37**, 2046), by oxidation of the metal, found Mo = 96·035.

Neodymium.—Baxter, Whitcomb, Stewart, and Chapin (*J. Amer. Chem. Soc.*, 1916, **38**, 302), by analyses of the chloride, find Nd = 144·27.

Columbium.—Smith and Van Haagen (*J. Amer. Chem. Soc.*, 1916, **38**, 1783), from the ratio between sodium columbate ($NaCbO_3$) and sodium chloride, find Cb = 93·13. The value 93·1 might be adopted in the table.

Argon.—Schultze (*Ann. Physik.*, 1915, [iv], **48**, 269) has redetermined the density of argon. The corresponding atomic weight is A = 39·945.

F. W. Clarke.
T. E. Thorpe.
G. Urbain.

1917.

International Atomic Weights.

	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	88·7
Zinc	Zn	65·37
Zirconium	Zr	90·6

LXVIII.—*The Valency of Two Directly Linked Nitrogen Atoms. Part I.*

By Bawa Kartar Singh.

In his observations (T., 1913, **103**, 604) on the inactivity of the free amino-group in the azonium compounds, the author put forward the hypothesis "that it is not possible for both the nitrogen atoms to become quinquevalent at the same time owing to steric interference or hindrance" (*loc. cit.*).

The present paper is a further attempt to adduce some more evidence in support of the same hypothesis.

According to Bischoff's "pyramid" formula for the space configuration of a quinquevalent nitrogen atom (Fig. 1),* the angle between any two adjacent negative valencies is less than a right angle, and that which the positive bond makes with each of the four negative bonds is greater than a right angle.† Now when two atoms of quinquevalent nitrogen are linked directly or

* For the sake of clearness, the lines representing all the valencies of the carbon atom and the negative valencies of the nitrogen atom in the accompanying figures 2 to 8 are shown black; the spheres representing nitrogen atoms and the line representing the positive valency of the nitrogen atom are coloured black and white; and the spheres representing the carbon atoms are shown white. In Fig. 1, the positive valency of the nitrogen atom is indicated by a thick broken line.

† Let a denote the length of the side of the square base of the pyramid, of height $4h$, and let A be equal to the angle between any two adjacent negative valencies, and B be equal to the angle which the positive bond makes with each of the four negative bonds; then $\cos A = \frac{2h^2}{a^2+2h^2}$ whence $A<\pi/2$; and $\cos B = -\frac{h}{\sqrt{h^2+\frac{a^2}{2}}}$ whence $B>\pi/2$. If we assume that the positive valency and the four negative valencies are all equal in length, then $a=4h$ (that is, the height of the pyramid becomes equal to the length of a side of the square base) and $\cos A = 1/9$, whence $A=83°37'$; and $\cos B=-1/3$, whence $B=109°28'$ (that is, the angle between the positive valency and each of the four negative valencies becomes equal to that between any two carbon valencies). Thus the position of the valencies can be fixed in space. The position of the five valencies, when they are all equal in length, may also be fixed graphically in the following way: Let the nitrogen atom be situated at the centre, O, of a sphere, radius r; draw a small circle (away from the pole X), perpendicular to the axis, at a distance $r/3$ below O. Take four equidistant points R_1, R_2, R_3, and R_4 on the small circle. Join OX, OR_1, OR_2, OR_3, and OR_4; then OR_1, OR_2, OR_3, OR_4 will represent the four negative valencies and OX the positive valency. The five atoms or groups will lie on the surface of a sphere at the centre of which the nitrogen atom itself will be situated.

indirectly, the result will be that the directions in space of the remaining valencies of one atom will either converge to, or diverge from, those of the other. In the former case steric hindrance will occur, and compounds of this type will be difficult to form, or not form at all; in the other case there will be no steric hindrance, and compounds of such a type should result, unless there is some other cause operating at the same time, as would be seen from the following cases.

Let two quinquevalent nitrogen atoms be directly linked by a negative valency of each (Fig. 2); the two negative valencies from each of the two nitrogen atoms will be inclined at an acute angle to the common bond; therefore the two negative valencies from the one nitrogen atom will either tend to meet or point to lines of shortest distance from those of the second nitrogen atom. This disposition of the bonds of the two atoms will constitute a source of steric hindrance. Consequently the second nitrogen atom cannot

FIG. 1

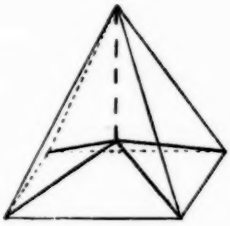
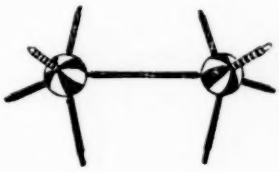


FIG. 2.



become quinquevalent, unless the groups are so small that the steric hindrance is almost ineffective. Instances of this are to be found in the dihydrochlorides of hydrazine, methylhydrazine, ethylhydrazine, and *as*-dimethylhydrazine. In these compounds the groups are small, and only one alkyl radicle (except in the case of dimethylhydrazine) is present. Even in the case of these bases the monohydrochlorides are much more stable than the dihydrochlorides. If we, however, increase the number of alkyl groups as well as their size, the dihydrochlorides cannot be obtained, as in the cases of *as*-diethylhydrazine, phenylmethylhydrazine, phenylethylhydrazine, phenylpropylhydrazine, etc. The latter compounds behave as monacidic bases, and will consequently combine only with 1 molecule of haloid acid to give salts of the type $RR_1\overset{III}{N}\cdot\overset{V}{N}H_3Cl$, in which there is only one quinquevalent nitrogen atom present.

If, however, a carbon atom is linked to a quinquevalent nitrogen atom through one of the negative valencies of the latter (Fig. 3), the remaining three valencies of the carbon atom will be directed

away from the remaining valencies of the nitrogen atom, since the angle which the common bond makes with any of the valencies of the carbon atom is 109°28′, and that which it makes with either of the adjacent negative valencies of the nitrogen atom is 83°37′ (see footnote, p. 780). This mutual disposition in space of the valencies of the two atoms cannot, therefore, produce any steric hindrance. Compounds of this type should therefore exist, and we have numerous instances of them in the substituted quaternary ammonium and azonium compounds.

Let us now consider the case in which a quinquevalent nitrogen atom is directly linked by its positive valency to a second quinquevalent nitrogen atom through one of the negative valencies of the latter (Fig. 4). The disposition of the four negative bonds of the nitrogen atom in this case, and that of the three carbon bonds discussed above (Fig. 3) with respect to the positive and the

FIG. 3.

FIG. 4.

remaining three negative bonds of the other nitrogen atom, are exactly identical, and therefore there is no steric hindrance in this case also. The compounds which would correspond with this type, namely, $R_4N{\cdot}NR_3Cl$, etc., are not yet known, but on the above analogy (Fig. 3) it may be predicted that ammonamide, $H_4N{\cdot}NH_2$, and its alkyl derivatives (also not known) would readily give stable salts of the types $H_4N{\cdot}NH_3Cl$, $R_4N{\cdot}NH_3Cl$, $R_4N{\cdot}NR_3Cl$, etc., in which the two directly linked nitrogen atoms are quinquevalent at the same time.

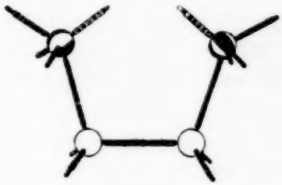
We may take another case in which two quinquevalent nitrogen atoms are separated by one or more methylene groups (Figs. 5, 6, 7). Compounds which correspond with this type may be represented by the general formula $ClR_3N{\cdot}[CH_2]_x{\cdot}NR_3Cl$, where x stands for 1, 2, 3, etc. The steric hindrance due to the disposition of the bonds which is present in the case of two directly linked nitrogen

atoms (Fig. 2) is absent here. Compounds of these types should therefore exist, and that such is actually the case is well borne out by experimental results (see pp. 785, 786).

The steric hindrance due to the disposition of the valencies in space is also absent if the two quinquevalent nitrogen atoms are directly joined by their positive valencies (Fig. 8), since all the

FIG. 5.

FIG. 6.



negative valencies of one nitrogen atom are directed away from those of the second nitrogen atom. Theoretically, therefore, compounds of this type should be formed, but none is known to exist, nor has the author been able to prepare any compound of the type $R_4N{\cdot}NR_4$, or even diammonium, $H_4N{\cdot}NH_4$, in which the alkyl groups are replaced by hydrogen atoms. Consequently, the non-

FIG. 7.

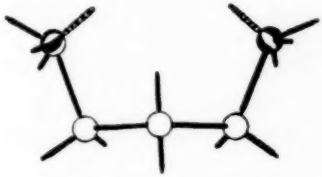


FIG. 8.

formation of compounds of this type is not due to steric hindrance, but to some other cause. That this cause is of an electrical nature is shown by the following consideration. In compounds of this type, $R_4\overset{(1)}{N}{\cdot}\overset{(2)}{N}R_4$, if the nitrogen atom numbered (1) is regarded as true "ammonium" nitrogen, the nitrogen atom numbered (2) becomes linked to five electropositive groups. No quinquevalent nitrogen compound containing five electropositive atoms or groups, however, is known; at least one halogen atom or another electronegative group is always present in these compounds.

The following experiments were devised with the object of testing the validity of this hypothesis:

(1) *The Action of Alkyl Iodides on Secondary Phenylalkylhydrazine Hydrochlorides.*

It has already been shown that methyl iodide does not react with phenylethylhydrazine hydrochloride, whereas under similar conditions it forms the substituted quaternary azonium iodide when mixed with the free base (*loc. cit.*). Similar negative results were also obtained in the present experiments in the action of methyl iodide and benzyl iodide on phenylpropylhydrazine hydrochloride, as well as in the action of ethyl iodide and benzyl iodide on phenylethylhydrazine hydrochloride. Under similar conditions the alkyl iodides and the free bases give the azonium iodides. These experiments clearly prove that although each of the α- and β-nitrogen atoms can become quinquevalent, both of them cannot be made so at the same time.

(2) *The Action of Halogen Acids on Azonium Haloids.*

It was hoped that the free amino-group of the azonium compounds $R_3\overset{V}{N}X\cdot\overset{III}{N}H_2$ would combine with a molecule of an halogen acid (HX_1) to form salts of the type $R_3\overset{V}{N}X\cdot\overset{V}{N}H_3X_1$, in which the β-nitrogen atom would also become quinquevalent, but all such attempts were unsuccessful. Moreover, as already shown (*loc. cit.*, p. 605), the platini- and auri-chlorides of the general formulæ $(R_3\overset{V}{N}\cdot\overset{V}{N}H_2,HCl)_2PtCl_6$ and $(R_3\overset{V}{N}\cdot\overset{V}{N}H_2,HCl)AuCl_4$ respectively are not produced; the compounds which are obtained contain the free amino-group, namely, $(R_3\overset{V}{N}\cdot\overset{III}{N}H)_2PtCl_6$ and $(R_3\overset{V}{N}\cdot\overset{III}{N}H_2)AuCl_4$.

(3) *The Action of Metals ("Molecular" Silver, Magnesium, Zinc) on Substituted Quaternary Azonium Haloids.*

The use of these metals in organic synthesis is well known. It was therefore expected that some of these metals may react on azonium haloids with the production of compounds containing two quinquevalent nitrogen atoms according to the following scheme:

$$2R_3NX\cdot NH_2 + 2M' = 2M'X + R_3(NH_2)\overset{V}{N}\cdot\overset{V}{N}(NH_2)R_3.$$

It is, however, found that this reaction cannot be brought about, since "molecular" silver does not act at all on the azonium haloids, whereas the action of magnesium and zinc is quite different, as shown below.

Magnesium and Zinc.—Both these metals act on the azonium haloids with the production of a tertiary amine and the liberation of ammonia. The mechanism involved in this reaction is somewhat obscure, but two interpretations of the change can be given. In the one case it may be assumed that magnesium first acts on the water (or an alcohol) with the production of magnesium hydroxide (or alkyloxide) and the liberation of hydrogen, and the latter element brings about the reduction thus:

$$R_3NX\cdot NH_2 + H_2 = R_3N + HX + NH_3.$$

A second possible explanation, which also does not appear to have been hitherto advanced, assumes the formation of a complex magnesium compound, as in Grignard's reaction, which is, however, immediately decomposed by water (or alcohol) present:

$$\begin{cases} \text{i. } R_3NX\cdot NH_2 + Mg = R_3N(MgX)\cdot NH_2 \\ \text{ii. } R_3N(MgX)\cdot NH_2 + H_2O = \underset{\text{Unstable.}}{R_3NH\cdot NH_2} + MgX\cdot OH \\ \text{iii. } R_3NH\cdot NH_2 = R_3N + NH_3 \end{cases}$$

Which of these two explanations is the correct one will be shown subsequently.

It may be pointed out that this reaction may be made the basis for the preparation of any tertiary amine. A substituted quaternary azonium haloid with the three suitable alkyl radicles may be prepared, which on being treated with magnesium (or zinc) in aqueous or alcoholic solution would give the corresponding tertiary amine in quantitative yield, according to the following generalised scheme:

$$C_6H_5\cdot \overset{V}{N}RR'I\cdot \overset{III}{N}H_2 + Mg(\text{or } Zn) + CH_4O(\text{or } H_2O) \longrightarrow NH_3 + C_6H_5\cdot NRR' + \text{basic salt of Mg (or Zn)}.$$

Incidentally, it may be remarked that the formation of the tertiary amines from the azonium haloids as above indicated is a clear proof of the structure of the latter compounds.

(4) *The Action of Alkyl Iodides on Ditertiary Hydrazines and other Ditertiary Nitrogen Bases.*

The comparison of the action of alkyl iodides on ditertiary hydrazines and other ditertiary nitrogen bases in which the two nitrogen atoms are directly linked with those in which they are separated by a sufficiently long chain of methylene groups would indeed furnish conclusive evidence in support or in refutation of the hypothesis. The following facts which support the hypothesis may be cited. The action of methyl iodide on phenylmethylhydrazine, phenylethylhydrazine (Singh, T., 1914, **105**, 1986; 1913, **103**, 607), and on phenyldimethylhydrazine, NMePh·NHMe (Harries, *Ber.*,

1894, **27**, 702), in which only one of the two nitrogen atoms is tertiary, leads to the formation of phenyldimethylazonium iodide, $NMe_2PhI \cdot NH_2$, phenylmethylethylazonium iodide,

$$NMeEtPhI \cdot NH_2,$$

and phenyltrimethylazonium iodide, $NMe_2PhI \cdot NHMe$, respectively. It is, moreover, found (compare Meyer and Jacobson, "Organische Chemie," Band II., p. 311) that the action of methyl iodide on phenyltrimethylhydrazine, $NMePh \cdot NMe_2$, in which both the nitrogen atoms are tertiary, results in the decomposition of the latter with the formation of dimethylaniline, and a fatty amine, but no diquaternary azonium compound is produced. The case is, however, different when the two nitrogen atoms are not directly linked, but are separated by a sufficiently long chain of methylene groups; both of them can then become quinquevalent at the same time as in the cases of the ethylenedikairolinium di-iodides (*Ber.*, 1903, **36**, 1163) and trimethylenebisphenylmethylethylammonium iodide (*Ber.*, 1910, **43**, 2707). These results are quite in harmony with the stereochemical conceptions put forward in the present paper (compare Figs. 2, 5, 6, 7). The same results will, no doubt, be obtained by the action of alkylene dibromides on monotertiary nitrogen bases. Experiments in this direction are still being continued.

Summary and Conclusions.

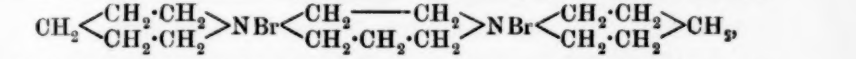
(1) Two quinquevalent nitrogen atoms cannot be linked by their negative valencies (except when the groups are very small, see p. 781). This inability is traced to a steric influence, arising from the disposition in space of the negative valencies themselves.

(2) Two quinquevalent nitrogen atoms cannot be linked by their positive valencies. This inability is not due to any steric hindrance, since all efforts to synthesise compounds of the type, $R_4\overset{(1)}{N} \cdot \overset{(2)}{N}R_4$, and more especially diammonium, $H_4\overset{(1)}{N} \cdot \overset{(2)}{N}H_4$ (in which this influence is clearly absent) have proved unavailing. The cause of this is, however, to be found in an electrical influence, namely, if the nitrogen atom numbered (1) is true "ammonium," the nitrogen atom numbered (2) becomes linked to five positive groups—an arrangement which is not capable of existence.

(3) On the other hand, it may be predicted that compounds containing two quinquevalent nitrogen atoms of the type $R_4N \cdot NR_3Cl$, etc., should exist. This result follows from the fact that the disposition in space of the remaining valencies of the two quinquevalent nitrogen atoms does not produce any steric hindrance (see p. 782).

(4) The consequences to which the above hypothesis leads are

very important from a stereochemical point of view. Extending the analogy which is found to exist between a single asymmetric carbon and nitrogen atom still further, it is to be expected that when two unlike asymmetric nitrogen atoms are simultaneously produced, four compounds would be formed, which would combine in pairs, or if the two asymmetric nitrogen atoms were similar, three compounds should be produced, as in the case of tartaric acid. It is evident from what has been said above, however, that since two directly linked asymmetric quinquevalent nitrogen atoms cannot be produced, the strict nitrogen analogues to the tartaric acids cannot be experimentally realised. Consequently, a complete analogy between the two elements is lacking. However, compounds in which the two asymmetric nitrogen atoms are separated by a sufficiently long chain of methylene groups ought to exist on this hypothesis. Instances in support of this may be found in the *cis-trans*-isomerides of ethylenetrimethylenedipiperidinium bromide,



obtained by Aschan (*Zeitsch. physikal. Chem.*, 1903, **46**, 293), and in the two optical isomerides obtained from the action of benzyl iodide on ethylenebis-*d*-conine (Wedekind and Ney, *Ber.*, 1913, **46**, 1895). The two inactive modifications of trimethylenebisphenylmethylethylammonium iodide (*loc. cit.*),

$$NMeEtPhI\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMeEtPhI,$$

must correspond with racemic and *i*-tartaric acids, and the resolution of one of them, which has hitherto resisted all attempts, would certainly establish the further analogy, in principle, between carbon and nitrogen atoms.

(5) Nitrogen heads the fifth group of the periodic classification. It is therefore natural to expect that the hypothesis and its deductions should also hold in the case of the remaining elements of this group, namely, phosphorus, arsenic, antimony, bismuth, vanadium, niobium, and tantalum, in the quinquevalent state.

Experimental.

Action of Methyl Iodide on Phenylpropylhydrazine Hydrochloride.

Phenylpropylhydrazine hydrochloride (1 gram), dissolved in the least possible quantity of chloroform, was treated with methyl iodide (0·8 gram). The mixture was at first cooled in ice, and was afterwards allowed to remain at the ordinary temperature for twenty-four hours without any crystals appearing; on the addition of a sufficient excess of ether, almost all the phenylpropylhydrazine hydrochloride used, melting at 146°, was recovered. A mixture of

the salt thus obtained with the original substance also melted at 146°. Thus no combination occurs between methyl iodide and phenylpropylhydrazine hydrochloride, whilst the azonium iodide is formed if the free base is mixed with methyl iodide under similar conditions.

It was similarly found that no combination occurs between benzyl iodide and phenylpropylhydrazine hydrochloride, benzyl iodide and phenylethylhydrazine hydrochloride, ethyl iodide and phenylethylhydrazine hydrochloride, whilst the corresponding azonium iodides are formed if the free bases are used under identical conditions.

Action of 'Molecular' Silver on Phenyldimethylazonium Iodide.

The azonium iodide (m. p. 126°) dissolved in methyl alcohol was treated with an excess of 'molecular' silver at the ordinary temperature. It was thus kept for twenty-four hours, during which time it was occasionally shaken. The silver was filtered off, and washed with methyl alcohol. The filtrate was allowed to evaporate in a vacuum desiccator, and almost all the solid substance melting at 126° was thus recovered. A mixture of this substance with the original compound also melted at the same temperature, which therefore proved the identity of the two substances. This clearly shows that 'molecular' silver has no action on phenyldimethylazonium iodide.

A second experiment, in which aqueous alcohol was substituted for methyl alcohol, gave identical results.

The following azonium iodides were also treated with 'molecular' silver in the above manner: phenyldiethylazonium iodide, phenyldibenzylazonium iodide, phenylmethylethylazonium iodide, and phenylbenzylpropylazonium iodide. In each case almost all the azonium iodide used was recovered unchanged, and its identity with the original substance was proved by the method of mixed melting points. These experiments clearly show that 'molecular' silver has no action on the azonium iodides.

Action of 'Molecular' Silver on Ammonium Chloride.

An aqueous solution of ammonium chloride containing a known amount of the salt was treated with an excess of 'molecular' silver at the ordinary temperature. The solid substance, recovered in the usual way, was found to be almost unchanged in amount. A chlorine estimation showed it to be pure ammonium chloride. (Found, Cl = 66·1. Calc., Cl = 66·35 per cent.) This proves that

'molecular' silver has no action on ammonium chloride, and that no diammonium is formed.

Action of Magnesium on Phenyldimethylazonium Iodide.

The azonium iodide (24 grams) dissolved in methyl alcohol was treated with excess of magnesium (the metal being added in three or four instalments) in a flask connected with a reflux condenser. An immediate action ensued, with the development of heat and abundant evolution of ammonia. At the same time a white precipitate of a basic magnesium salt was formed. In the beginning the flask was cooled in order to moderate the reaction, which, near the end, was completed on the water-bath. The methyl alcohol was distilled off, and the residue repeatedly extracted with ether. The extract was thoroughly washed with water, dried over solid potassium hydroxide, the ether removed by distillation, and on submitting the residue to fractional distillation, 9·2 grams of the base (theory requires 11 grams), boiling at 193°, were obtained. This yield corresponds with 84 per cent. of the theoretical. The base was proved to be identical with dimethylaniline by its boiling point and by the preparation of derivatives, as shown in the following table:

	Base.	Dimethylaniline.
Boiling point	193°	193°
Picrate, m.p.	163—164°	163—164°
Phenylbenzyldimethylammonium iodide, m p.	164°	165°

(Jones, T., 1903, **83**, 1409).

A mixture of the picrate from the base thus obtained and that from dimethylaniline showed no lowering in the melting point.

The picrate was analysed with the following result: Found, N=16·21. Calc., N=16·0 per cent. Komatsu (*Mem. Coll. Sci. Eng., Kyoto Imp. Univ.*, 1912, **3**, 371) gives lower values for the melting points of the picrate (154—155°) and phenylbenzyldimethylammonium iodide (141—142°). As the melting points of the latter compound found by the present author and Jones (*loc. cit.*) are concordant, it is probable that the dimethylaniline used by Komatsu was impure.

The ammonia which was evolved by the action of magnesium on the azonium iodide was identified by its odour, etc., as well as by absorbing it in hydrochloric acid and converting it into the platinum salt. (Found, Pt=43·84; N=6·29. Calc., Pt=43·95; N=6·30 per cent.)

In aqueous solution the action of magnesium was less energetic. With zinc, the action, although slow, was similar to that with

magnesium, and the picrate from the resulting base had the same melting point (163—164°).

Action of Magnesium on Phenyldiethylazonium Iodide.

The azonium iodide dissolved in methyl alcohol was treated with magnesium, when, as usual, heat was developed and ammonia liberated. In aqueous solution there is less development of heat, and the action is somewhat slower. The diethylaniline produced was separated in the usual way, and converted into the picrate, consisting of yellow prisms, melting at 142°, and not at 135—136°, as stated by Komatsu (*loc. cit.*). (Found, N = 14·55. Calc., N = 14·81 per cent.) The picrate obtained from pure diethylaniline had identical melting point and other properties. A mixture of the two picrates also melted at 142°.

With zinc, the products were identical, although the action was slow.

Action of Magnesium on Phenylmethylethylazonium Iodide.

Magnesium dissolves in a methyl-alcoholic solution of the azonium iodide with considerable development of heat and evolution of ammonia. In aqueous solution the reaction was less rapid, and no appreciable amount of heat was developed. The base, methylethylaniline, was converted into the picrate, consisting of greenish-yellow prisms melting at 134—135°, and not at 124—125°, as stated by Komatsu (*loc. cit.*). (Found, C = 50·05; H = 4·97; N = 15·03. Calc., C = 49·46; H = 4·4; N = 15·39 per cent.) The yield of the picrate was about 70 per cent. of the azonium iodide used. When zinc was employed, the products were similar, but the action was less rapid.

Action of Magnesium on Phenylbenzylmethylazonium Iodide.

The base, benzylmethylaniline, was isolated in the usual way, and was converted into its picrate, which consisted of yellow, rhombic prisms melting at 109°, and not at 101—101·5°, as recorded by Komatsu (*loc. cit.*). (Found, C = 56·65; H = 4·67; N = 12·78. Calc., C = 56·34; H = 4·23; N = 13·15 per cent.) Benzylmethylaniline picrate prepared from pure benzylmethylaniline and picric acid when mixed with the above picrate produced no lowering of the melting point.

Action of Magnesium on Phenylmethylpropylazonium Iodide.

This and the following azonium iodide are new substances, and will be described later.

The base, methylpropylaniline, isolated in the usual way, was

converted into the picrate, which appeared in yellow prisms, melting at 106—107°, and not at 103—104°, as stated by Komatsu (*loc. cit.*) (Found, N = 15·32. Calc., N = 14·81 per cent.)

Action of Magnesium on Phenylbenzylpropylazonium Iodide.

The base, benzylpropylaniline, was the result of the action of both magnesium and zinc on a methyl-alcoholic solution of the azonium iodide with the usual evolution of ammonia. It was converted into the *picrate*, consisting of yellow prisms and melting at 145—146°. A mixture of the picrates, obtained from the action of the two metals, produced no lowering of the melting point:

0·0420 gave 4·9 c.c. N_2 (moist) at 30° and 766 mm. N = 12·77.

$C_{16}H_{19}N,C_6H_3O_7N_3$ requires N = 12·33 per cent.

This base does not appear to have been hitherto known. It will be described more fully subsequently.

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[*Received, April 10th*, 1916.]

LXIX.—*The Volatile Oil from the Wood of the Indian Deodar Tree.*

By OSWALD DIGBY ROBERTS.

THE deodar tree is widely distributed in Northern India, and is a native of the Western Himalaya. The timber is now being used for conversion into railway sleepers, and in the process a good deal of waste wood is produced, which, it has been suggested, might be utilised for the distillation of volatile oil, just as the waste wood from the "pencil cedars" of Florida and East Africa is employed for the manufacture of cedar wood oil.

The botanical relationships of the deodar are not yet fully worked out. Some authorities regard it as a definite species, *Cedrus Deodara*, Loud., whilst others consider it to be a variety of *C. Libani*, Barr. The genus Cedrus includes two other well-known species or geographical varieties of *C. Libani*, namely, the Atlas cedar, *C. atlantica*, Manetti, and the Cyprus cedar, *C. brevifolia*, Elwes and Henry. The volatile oil from the wood of the Atlas cedar has been examined by Grimal (*Compt. rend.*, 1902, **135**, 582, 1057).

Deodar wood oil has been already examined by Schimmel & Co. (*Geschäftsber.*, Oct., 1914–April, 1915), who recorded its constants and isolated from it a ketone, apparently identical with that found in Atlas cedar wood oil by Grimal (*loc. cit.*), but were unable to identify the sesquiterpene, also present, with cadinene, which Grimal (*loc. cit.*) isolated from the Atlas cedar oil he examined.

The two samples of deodar oil examined by the author were received at the Imperial Institute from the Forest Economist to the Government of India in 1914 and 1915 respectively.

Both samples of oil were of reddish-brown colour, and possessed a characteristic balsamic odour. They had the following constants:

	(I).	(II).
D_{15}^{15}	0·9549	0·9756
α_D^{22} in a 100 mm. tube	+52°16′	+34°6′
n_D^{21}	1·5195	1·5225
Acid value	5·6	4·5
Ester value.....	19·3	4·9
,, after acetylation.	30·8	34·4
Solubility in 90 per cent. alcohol	Not soluble in 20 or less volumes.	Miscible in all proportions.

The following fractions were obtained when the oils were distilled under atmospheric pressure:

Fraction.	Boiling point.		Sample (I).	Sample (II).
		Per cent.	16	8
1	230—260°	D_{15}^{15}	0·9605	0·9472
		α_D^{22}	+40°12′	+29°0′
		Per cent.	25	16
2	260—270°	D_{15}^{15}	0·9467	0·9439
		α_D^{22}	+53°15′	+27°44′
		Per cent.	47	24
3	270—280°	D_{15}^{15}	0·9466	0·9482
		α_D^{22}	+41°12′	+26°18′
		Per cent.	10	35
4	280—310°	D_{15}^{15}	0·9419	0·9634
		α_D^{22}	—	+18°33′
Residue		Per cent.	2	17
		D_{15}^{15}	—	1·0821

Description of Fractions.

Fraction 1 was of pale yellow colour and contained a ketone the odour of which characterised the original oil. With ferric chloride this fraction gave a blood-red coloration due to the presence of a

phenol (see p. 794). Fractions 2 and 3 were bright yellow in colour, somewhat viscous, and possessed very little odour. In the case of the first sample, fraction 4, which was dark brown and very viscous, deposited some crystals on keeping; these proved to be stearic acid, resulting probably from the decomposition of an ester.

Isolation of a Ketone, $C_9H_{14}O$.

This ketone, which does not combine with alkali sulphites, was isolated from fraction 1 by means of its semicarbazone, which after several crystallisations from alcohol was obtained in colourless, glistening leaflets melting at 163—164°:

0·1895 gave 0·4282 CO_2 and 0·1492 H_2O. C = 61·6; H = 8·7.
0·1396 „ 0·3159 CO_2 „ 0·1100 H_2O. C = 61·7; H = 8·7.
$C_{10}H_{17}ON_3$ requires C = 61·5; H = 8·7 per cent.

The ketone in fraction 1 reacted with hydroxylamine to form an oxime which could not be obtained in a solid condition, but combined with bromine, producing a solid dibromo-oxime melting at about 130°. The ketone has an odour recalling that of amyl acetate, and is probably *p*-methyl-Δ^3-tetrahydroacetophenone. The latter substance has not been identified previously as a constituent of a volatile oil, but is obtained by the oxidation of β-terpineol (Stephan and Helle, *Ber.*, 1902, **35**, 2151). According to these authors the odour of this ketone somewhat resembles that of amyl acetate; the ketone has b. p. 68·5—70°/4 mm., D^{15} 0·9435, n_D^{15} 1·4742, and its semicarbazone forms colourless leaflets melting at about 160°.

Decomposition of the semicarbazone by dilute sulphuric acid and distillation with steam yielded, however, as chief product, not the original ketone, but a fraction boiling at 222—224° (uncorr.), which had n_D^{20} 1·4965, and furnished a semicarbazone melting at 204—205°. This appeared to be *p*-tolyl methyl ketone, and this conclusion was confirmed by the production from it of bromoform boiling at 151°, and *p*-toluic acid melting at 178—179°, by oxidation with a 4 per cent. alkaline bromine solution. The acid obtained did not depress the melting point of pure *p*-toluic acid, and was oxidised by potassium permanganate to terephthalic acid, leaving no doubt as to its identity with *p*-toluic acid. This ketone is apparently identical with that isolated by Grimal from oil of *Cedrus atlantica* (*loc. cit.*), which gave a semicarbazone (m. p. 159—160°) and a dibromo-oxime (m. p. 132—133°).

Isolation of a Phenol.

Having removed from the original oil by treatment with dilute sodium carbonate solution a small quantity of free acids which appeared to consist mainly of acetic acid, the phenols were separated from the oil with a 5 per cent. solution of sodium hydroxide, the amount obtained corresponding with 0·4 per cent. on the original oil. The substance possessed a sweet, phenolic odour, and was almost insoluble in water. It produced a deep blood-red coloration with ferric chloride in alcoholic solution, and yielded a benzoyl derivative, which crystallised from dilute alcohol in small, slender needles melting at 70°. No phenol with these properties appears to have been recorded as a constituent of a volatile oil. As the second sample of oil contained less than 0·1 per cent. of this phenol, further investigation was not possible.

Hexoic, Heptoic, and Stearic Acids resulting from the Hydrolysis of the Oil.

After having freed the original oil from acids and phenols, it was digested on the water-bath for two hours with excess of *N*/2-alcoholic potassium hydroxide. The product was shaken with a large excess of brine, and the clear aqueous liquid separated from the oily portion and submitted to steam distillation in order to remove the alcohol together with traces of oil. The residue from the above distillation was acidified with dilute sulphuric acid, steam again passed in, and the distillate collected in three fractions. In fractions 1 and 2 insoluble acids had separated, but fraction 3 contained very little acid; the odour of fraction 1 resembled that of *n*-hexoic acid. Silver salts prepared from these fractions by precipitation gave the following percentages of silver:

Fraction 1: 0·1106 gave 0·0540 Ag. Ag = 48·8.
$C_6H_{11}O_2Ag$ requires Ag = 48·4 per cent.

Fraction 2: 0·0612 gave 0·0278 Ag. Ag = 45·5.
$C_7H_{13}O_2Ag$ requires Ag = 45·5 per cent.

Hence these volatile acids would appear to consist of a mixture of hexoic and heptoic acids.

The oily residue remaining after the saponification, and precipitated by the brine, was semi-solid owing to the presence of sodium salts of higher fatty acids. It was shaken repeatedly with successive quantities of water rendered slightly alkaline with potassium hydroxide, and from the combined aqueous extracts the acids were liberated by dilute sulphuric acid. The crude product was dissolved in hot alcohol, which on cooling deposited stearic acid in

crystalline laminæ melting at 71°. The acid was converted into the silver salt, of which 0·02119 gave 0·0585 Ag; Ag=27·60. (Stearic acid melts at 69·3—71·5° according to different investigators, and silver stearate contains Ag=27·62 per cent.) The neutralised mother liquor from which the stearic acid had separated was submitted to fractional precipitation with alcoholic silver nitrate. The silver salt was in each case reprecipitated to free it from impurities which were present in appreciable quantity. The various fractions gave the following results on analysis:

1st precipitation:	0·1308 gave	0·0361 Ag.	Ag=27·59 per cent.		
2nd „	0·1416 „	0·0390 Ag.	Ag=27·54 „	„	
3rd „	0·1270 „	0·0335 Ag.	Ag=26·37 „	„	
4th „	0·1950 „	0·0520 Ag.	Ag=26·66 „	„	

The decreased percentages of silver obtained in fractions 3 and 4 are due probably to contamination of the silver salt with non-acid impurities rather than to the presence of some other acid.

The second sample of the deodar oil contained a relatively small percentage of esters, and no esters of stearic acid were found.

Isolation of a Sesquiterpene.

The principal constituents of this oil are sesquiterpenes, which appear to be associated with a variable amount of sesquiterpene alcohols, a high proportion of the latter being indicated by a marked increase in the gravity of the oil, a greater solubility in 90 per cent. alcohol, and also a correspondingly higher acetylation value (compare constants of samples I and II on p. 792). Having freed the original oil from free and combined acids and phenols by treatment with alcoholic potassium hydroxide, it was distilled under atmospheric pressure, and the portion boiling between 250° and 280°, which constituted the bulk of the oil, collected separately. After prolonged treatment with sodium, with many distillations under diminished pressure, the greater part of the product was found to consist of a fraction which boiled at 151—153°/19 mm. or 262—265° (uncorr.) atmospheric pressure. This fraction was a colourless, mobile liquid, and had D_{15}^{15} 0·9319, α_D^{23} +16°51′, n_D^{13} 1·5150. (An otherwise similar fraction obtained from the first sample of oil had α_D^{22} +58°34′). Its solution in glacial acetic acid produced a characteristic colour reaction with concentrated sulphuric acid similar to that of cadinene:

0·1883 gave 0·6036 CO_2 and 0·1949 H_2O. C=87·4; H=11·5.

$C_{15}H_{24}$ requires C=88·2; H=11·7 per cent.

As it was not, apparently, entirely free from oxygen, the fraction was distilled over phosphoric oxide in order to determine whether

this would produce any alteration in its physical properties. The product which boiled at the same temperature now had D_{15}^{15} 0·9276, α_D^{20} +14°36′, n_D^{20} 1·5170, and 0·1363 gave 0·4399 CO_2, and 0·1424 H_2O. C = 88·0; H = 11·6 per cent.

Attempts to prepare solid derivatives of this sesquiterpene were unsuccessful. Hydrogen chloride was absorbed with avidity when passed into a cooled ethereal solution, and when after keeping for some days the ether was evaporated, most of the combined hydrogen chloride was thereby expelled. The residue distilled at 145—155°/10 mm., and the colourless oil thus obtained had D_{15}^{15} 0·956 and contained only 4·9 per cent. of chlorine:

$C_{15}H_{24}$,HCl requires HCl = 15·17 per cent.

Summary.

The composition of the volatile oil from the wood of *Cedrus Deodara*, Loud., as indicated by the results of this investigation, is as follows:

	Per cent.
A *ketone*, $C_9H_{14}O$, probably methyl-Δ^3-*p*-tetrahydroacetophenone	about 2
A *phenol* undetermined	from 0·07 to 0·4
Esters of hexoic, heptoic, and stearic acids	from 3 to 12
Sesquiterpenes: consisting chiefly of a *d*-sesquiterpene of variable rotation	from 50 to 70

Sesquiterpene Alcohols.—These appeared to constitute the remainder of the oil, associated with high boiling, viscous, decomposition products.

Scientific and Technical Research Department.
Imperial Institute, [*Received, July 20th*, 1916.]

LXX.—*Studies in Catalysis. Part V. Quantitative Expressions for the Velocity, Temperature-coefficient, and Effect of the Catalyst from the Point of View of the Radiation Hypothesis.*

By William Cudmore McCullagh Lewis.

The well-known fact that the velocity of an ordinary or thermal reaction is very sensitive to changes in temperature indicates that ultimately velocity and temperature are due to a common cause, both being manifestations of a certain mode of distribution of heat energy, characteristic of the material system in question. It has long been recognised that the influence of temperature on reaction-

velocity cannot be accounted for simply on the basis of an increase in the kinetic energy of the molecules as a whole, for in the most favourable case this increase could not account for more than 1 per cent. of the observed effect, and it is doubtful whether the change so produced would be even qualitatively in accord with that observed. It is evident, therefore, that the effect of temperature has to do, not with the kinetic energy of the molecule, but with its internal energy. By treating the problem of reaction-velocity from the point of view of statistical mechanics it is possible to correlate the velocity-constant with the temperature, as has been done by Marcelin and by Rice (*Rep. Brit. Assoc.*, 1915, p. 397), the quantitative relation being expressible thus:

$$d \log k / dT = E / RT^2.$$

In deducing this expression it has been assumed that a molecule reacts when its internal energy has been raised to a certain critical value, the term E denoting the difference between this critical value and the mean or average internal energy reckoned per gram-molecule. E may therefore be called the critical increment. In thus defining E, a small term has been omitted, which is negligible, in general, compared with the two mentioned. This expression being of the same type as the empirical equation of Arrhenius, namely, $d \log k / dT = A / RT^2$, which is known to be very generally applicable, it follows that the Marcelin-Rice expression reproduces experimental results in a satisfactory manner. Any deduction based on statistical mechanics resembles a thermodynamical deduction, in that, being deduced on a quite general basis, the result is a trustworthy one. On the other hand, it is obvious that the mode of deduction in this case does not suggest any mechanism whereby the increase in energy from the mean value to the critical value is brought about. In order that further progress may be made in chemical kinetics it is therefore necessary to supplement the result obtained by Marcelin and by Rice. Three years ago the idea suggested itself to the author that possibly the infra-red radiation which was necessarily present throughout any system in virtue of its temperature may be the active agency in promoting chemical change of the ordinary or thermal type, such changes including not only the so-called uncatalysed reactions, but catalysed reactions as well, in so far at least as these are met with in homogeneous systems, and further that the influence of temperature on velocity might be explained on the same basis. It was later recognised that this hypothesis was quite consonant with the treatment adopted by Marcelin and by Rice. The hypothesis, in fact, appeared to be one of the possible modes of supplementing and extending the purely dynamic view.

Briefly, the hypothesis is that the increase in internal energy

which a molecule must receive before it is capable of reacting (that is, the critical increment E) is communicated to it by infra-red radiant energy present in the system, the addition of energy being made in terms of quanta of the absorbable type. If it be effected by a single quantum it may be easily shown that the quantum corresponds with a wave-length in the short infra-red region, a region in which many substances exhibit absorption (T., 1914, **105**, 2338; 1915, **107**, 243). The principal feature of the hypothesis is the introduction of the quantum theory into the problem of chemical kinetics, the effect of temperature, and catalysis. The necessity of restricting ordinary chemical reactivity to the infra-red region is due to the fact that at the ordinary temperature, as is well known, the greater part of the radiation present in the system is of the infra-red type, and, in order that any of Planck's relations may be employed, it is essential that temperature radiation alone be considered, and further that the radiation and the matter composing the system be in temperature equilibrium. On Planck's view, the interchange between matter and radiant energy is effected through the medium of oscillators, situated on the molecules of the matter present. In the case of photochemical reactions as ordinarily carried out the temperature of the radiation is much higher than that of the system on which the radiation acts. To such cases Planck's expressions do not apply. It is necessary to emphasise this point, as it is not generally recognised that there is this fundamental distinction to be drawn between thermal and photochemical processes. In the case of thermal reactions occurring at a constant temperature in a thermostat, which defines the temperature of the system, both with regard to matter and radiation, Planck's theory may be applied with some degree of certainty. In this connexion the following statement made by Planck ("Theory of Heat Radiation," Eng. ed., p. 7) is of importance: "A special case of temperature radiation is the case of the chemical nature of the emitting substance being invariable. Nevertheless, it is possible, according to what has been said, to have temperature radiation while chemical changes are taking place, provided the chemical condition is completely determined by the temperature."

That radiation in general may bring about chemical change has long been known. Further, the idea that infra-red radiation may be the cause of ordinary or thermal reactions appears first to have been suggested in a general way by Trautz in 1906, based on the analogy to short wave or photochemical reactions. The suggestion made by Trautz did not lead, however, to any quantitative results. in 1911 Krüger (*Zeitsch. Elektrochem.*, 1911, **17**, 453) suggested that infra-red radiation was the cause of such effects as solution

pressure, dissociating power of a solvent, electrolytic dissociation, and solubility of a solute. Krüger has not considered the question of the rate of reactions, and the influence of temperature and of catalysts on the rate.

In the previous papers of this series (Part I., T., 1914, **105**, 2330; Part II., T., 1915, **107**, 233; Part III., T., 1916, **109**, 55; Part IV., T., 1916, **109**, 67) the effect of temperature and the function of catalysts in a homogeneous system have been considered from the point of view of the quantum theory, and the experimental evidence brought forward, although of a preliminary nature, is considered sufficient to justify the attempt at this stage to give to the hypothesis already employed a more quantitative form.* An elementary treatment of the problem has already been given by the author (*Rep. Brit. Assoc.*, 1915, p. 394), and it is proposed in the present paper to extend these considerations to the influence of the medium in which the reaction proceeds, and to the effect of the catalyst on the value of the temperature-coefficient. The closely allied problems of the equilibrium-constant, its variation with temperature in relation to the heat of the reaction, and the anomaly of strong electrolytes have also been considered from the point of view of the radiation hypothesis, and will be communicated later.

Conditions for Reactivity on the Radiation Hypothesis.

According to the law of mass action the reactivity of a substance is measured by its active mass. Since the time of Guldberg and Waage it has been considered sufficient to regard the concentration of the substance as an accurate measure of the active mass, and this has been borne out by an accumulation of experimental results, which serve to demonstrate the general truth of the hypothesis. At the same time certain discrepancies have been observed (mainly as the result of electromotive measurements), which indicate that concentration *per se* is not the only factor determining reactivity, except as a limiting case. To attempt to modify the proportionality between active mass and concentration it is necessary to take into account the energy exchanges which accompany, or rather precede, molecular change, for as the fact of a *finite* velocity demonstrates, all the molecules of a system are not at any one moment in the same reactive state. From what has already been

* This is the more necessary as physico-chemical changes viewed from the quantum point of view are receiving attention from other workers, for example, Heydweiller: "Quantum Theory and Heat of Neutralisation," (*Ann. Physik*, 1915, [iv], **48**, 681). Andersen: "An Application of the Quantum Theory to the Speed of Reaction in Monomolecular Reactions," (*Oversigt. Kgl. Dansk. Vidensk. Selsk. Forh.*, 1915. p. 225).

said regarding the absorption of energy by an average molecule to bring its energy content to the critical value, it will be evident that the amount and nature of the radiation present in the system must play a definite part in the reactivity of a given species. From this point of view, therefore, the active mass of a species is not simply proportional to its concentration, but is simultaneously dependent on the radiational environment, the observed reactivity being due to the product of these two effects. The active mass is, in fact, identical with the number of molecules brought per second into the active state by means of the radiation present in the system. The fundamental assumption is that the radiational environment can be identified with the radiation density of the absorbable type present throughout the system. That is, the active mass of a species, spontaneously decomposing, is proportional to its concentration, multiplied by the radiation density of the type which the substance can absorb, the radiation being present in virtue of the temperature of the system. The radiation density, u_ν, is the amount of radiation made up of quanta corresponding with a certain frequency ν, which is present in unit volume of the system, when the radiation and the matter are in thermal equilibrium. If the radiation density is too small the substance will not react, howsoever great its concentration may be. On this view the function of the positive catalyst (added catalyst or solvent) is to increase the radiation density of the type absorbable by the reactant, whereby a greater number of the molecules of the reactant attain the critical value for their internal energy per second, with the result that the reaction-velocity is increased. It is evident that the optimum condition for the transfer of a quantum from a catalyst individual to a molecule of reactant occurs when the two are in contact, and this, according to the theory of probability, is proportional to the product of the concentrations of the reactant and catalyst. Hence when a catalyst is present in the system the active mass of the reactant may be written proportional to its concentration, multiplied by the concentration of the catalyst, multiplied by the radiation density u_ν. It may be well to point out that these considerations deal with a possible mechanism whereby a given species is made reactive. The question of the chemical nature of the actual reactive species does not enter directly. The formation of intermediate compounds, solvates, or complexes containing reactant and added catalyst, for which, in general, there is considerable experimental evidence, is not precluded in this method of treatment. The considerations deal with a general mode, whereby the molecular structure, whatever it may be, may exhibit reactivity.

Radiation Density.

On the basis of the quantum theory the radiation density, u_ν, corresponding with a certain frequency ν, is given by the expression:

$$u_\nu = \frac{8\pi h\nu^3 n^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1},$$

where h = Planck's constant.

$h\nu$ = quantum of radiant energy corresponding with the frequency ν.

n = refractive index of the system for the region which contains ν.

c = velocity of light in a vacuum.

k = gas constant per molecule, that is, $R = Nk$, where R is the gas constant per gram-molecule, and N is the number of molecules in one gram-molecule.

T = absolute temperature.

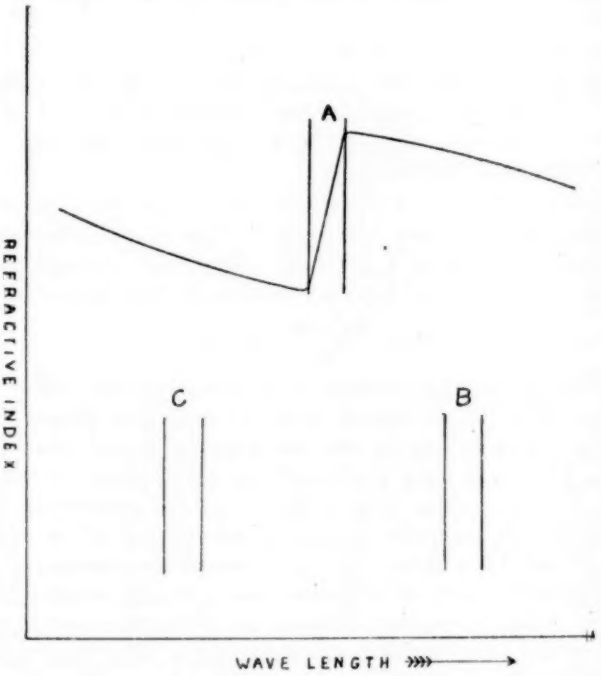
As already pointed out (*Rep. Brit. Assoc., loc. cit.*), the region of importance for chemical reactivity is the short infra-red. The corresponding values of ν are such that $e^{h\nu/kT} - 1$ becomes $e^{h\nu/kT}$. Hence we may write the above expression in the simpler form:

$$u_\nu = \frac{8\pi h\nu^3 n^3}{c^3} \cdot e^{-h\nu/kT}.$$

In this form Planck's expression is in agreement with Wien's radiation law. It will be observed that the radiation density is determined by the frequency ν, the temperature T, and the refractive index n. The latter term is of particular significance for the present purpose, for, in dealing with radiation of the absorbable type, we are dealing with radiation in the neighbourhood of an absorption band. It has been shown to be a necessary consequence of the electromagnetic theory of radiation that n should exhibit a marked change in value in passing through an absorption band, and this conclusion has been verified experimentally. The verification will be referred to later. For wave-lengths just longer than that of the band, the value of n is abnormally great; for wave-lengths just shorter than the band, n is abnormally small. It is evident that the radiation density itself must show a similar change to an enhanced degree, since u_ν varies as the cube of the refractive index. An enhanced radiation density means that the number of quanta corresponding with the wave-length region just below the band are present in abnormally large amount throughout the system. It is a remarkable conclusion from the electromagnetic theory that the radiation density corresponding with the centre of the band is not abnormally increased. This has an important bearing on the

stability of substances, as will be pointed out later. The variation with wave-length of the index n of a substance A having an absorption band at the position A is shown diagrammatically in the figure.

The distribution of radiant energy which corresponds with this variation of n also serves to explain, in a general way, the influence of the radiation from one substance on another. Suppose that a second substance B is likewise present in the system, having an absorption band, as indicated, at a somewhat longer wave-length than that of A. It is clear that the molecules of B are lying in a



region very rich in quanta of the type which they, the B molecules, can absorb. The substance A has therefore the effect of increasing the reactivity of B by increasing its internal energy. In other words, the substance A is acting as a positive catalyst as regards B. It may cause B either to decompose or to fluoresce further in the infra-red. On the other hand, A has no catalytic effect on another substance, C, for the band of the latter occurs at a region at which the temperature radiation as modified by the presence of A is abnormally small. C can, however, act as a positive catalyst with respect to A. Even in those cases in which catalytic effects as

such are not regarded as coming into play, the interaction of two different kinds of molecules may be attributed to the modification in the distribution of the infra-red radiation produced by one of the species and exerted on the other.* From the point of view of the radiation hypothesis, therefore, there is no distinction, as regards the initial step, between a catalytic and a stoicheiometric effect. Further, as temperature rises, although n only varies slightly, the expression for u_ν contains T as an exponential, and therefore the radiation density increases rapidly with the temperature. This is qualitatively in agreement with the effect of temperature on the reaction velocity. It will be shown later that the increase in radiation density accounts quantitatively for the temperature-coefficient of chemical reactions. That the relative positions of the absorption bands is sufficient to explain the negative catalytic effect of water in the hydrolysis of methyl acetate has already been pointed out in Parts III. and IV. of this series.

Referring again to the figure, it will be observed that the value of n, and therefore of u_ν, is not abnormally increased at the centre of the band itself. That is, the molecules of A cannot exert any marked autocatalytic effect on themselves, except as a second order magnitude. To this we may attribute the stability of pure substances, as well as the fact that the law of mass action holds at all, for according to this law the rate of decomposition in a unimolecular reaction is proportional to the first power of the concentration. Except at high temperatures, it is doubtful whether any reaction, especially a unimolecular reaction, proceeds without a catalysing agent, for in such cases the decomposition would have to depend on a normal, and not on an enhanced density of radiation. The results of experiments with carefully purified gases would appear to bear this out. From the same point of view it may be suggested that substances of very similar constitution, and therefore possessing almost identical absorption spectra, would not readily react with one another, as, for example, in the case of mixtures of hydrocarbons, of esters, or of alcohols, etc.

In those cases, therefore, in which a reaction proceeds without any catalytic or mutual effect—and such a reaction must obviously be unimolecular—the active mass, and therefore the rate, depend on the concentration and the radiation density u_ν' due to the temperature. In the more general case, however, when a multimolecular reaction is involved, or when a catalyst is present, either as

* To denote this active and passive relationship between, say, A and B, it is convenient to call A the *excitor* and B the *receptor*, these terms being used to distinguish them from others such as actor, acceptor, and inductor, which are already employed in a somewhat different sense (compare Mellor, "Statics and Dynamics," p. 334).

an additional solute or as the solvent itself, the active mass is proportional to the concentration of the reactant, multiplied by the concentration of the catalyst, multiplied by the radiation density u_ν.

Unimolecular Reaction-velocity in a Gaseous System in the Absence of a Catalyst.

The active mass in this case has been defined as proportional to the product of the concentration into the radiation density u of the frequency absorbed. In general, a substance possesses more than one absorption band in the infra-red, and energy may be added to the molecule at more than one position. To simplify the treatment we shall consider a single frequency ν as being the effective frequency. If a is the initial concentration of the reactant and x is the amount transformed after time t, the velocity is given by:

$$dx/dt \propto (a-x)u_\nu \propto (a-x)\frac{8\pi h\nu^3 n^3}{c^3} \cdot e^{-h\nu/kT}.$$

Since the effect of temperature is now explicitly allowed for, it is probable that the proportionality factor required is independent or nearly independent of the temperature. Also $8\pi h\nu^3/c^3$ is necessarily a constant for a given reaction, and the refractive index n, in the case of a gaseous reaction, is so nearly unity that it may likewise be regarded as a constant throughout the course of the reaction. A determination of n in the infra-red region has recently been made in the case of a gas (carbon dioxide) by Statescu (*Phil. Mag.*, [vi], 1915, **30**, 737), using the gas as a prism. The range of wave-lengths examined extends from 0·5894 μ to 13·19 μ. A band occurs at 4·270 μ. At 5 μ $n=1{\cdot}000531$, and at 4 μ $n=1{\cdot}000289$. These are the maximum and minimum values of n observed by Statescu, although it is impossible to state whether they represent the limiting values or not. It is evident, however, that the assumption that n may be regarded as unity in a gaseous system is sufficiently exact for the present purpose. Retaining the quantity n^3 in the expression and collecting the other constants, including the proportionality factor under the symbol P, we can write:

$$dx/dt = P(a-x)n^3 \cdot e^{-h\nu/kT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At constant temperature this expression becomes identical with the ordinary mass action equation. On integration we obtain:

$$\frac{1}{t}\log\frac{a}{a-x} = P \cdot n^3 \cdot e^{-h\nu/kT} \quad . \quad . \quad . \quad . \quad (2)$$

But $1/t \log a/a-x = k_{\text{obs.}}$, where $k_{\text{obs.}}$ is the experimentally determined velocity constant. Hence:

$$k_{\text{obs.}} = P \cdot n^3 \cdot e^{-h\nu/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To find the effect of temperature on the velocity-constant it is convenient to differentiate the log. of equation (3), thereby obtaining the relation:

$$\frac{d\log k_{obs.}}{dT} = \frac{h\nu}{kT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

But k, the gas constant per molecule, can be written as R/N, where N is the Avogadro number. Hence:

$$\frac{d\log k_{obs.}}{dT} = \frac{Nh\nu}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The term $Nh\nu$ is a constant, characteristic of a given substance, and independent of temperature for considerable temperature intervals. It may therefore be denoted by the symbol A, whence:

$$\frac{d\log k_{obs.}}{dT} = \frac{A}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This expression is identical in form with the empirical relation of Arrhenius, which has been shown to be in agreement with experiment for reactions of very varied type. The fact that this relationship can be obtained on the basis of the radiation hypothesis constitutes the most direct evidence in support of the hypothesis.

Equation (5) is also of significance when considered in conjunction with the relation of Marcelin and of Rice, namely,

$$\frac{d\log k}{dT} = \frac{E}{RT^2},$$

where E is the critical increment, that is, the amount of energy which must be contributed to one gram-molecule of the substance to bring it from the mean state to the reactive state. On comparing the two equations and equating like terms, it follows that $E = Nh\nu$

or

$$E/N = h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

But E/N represents the amount of energy which has to be added to a single molecule to make it react, and this is, therefore, by the above relation, one quantum. This is simply a statement of the Einstein law of the photochemical equivalent, which is now shown to be applicable to reactions caused by radiation of the short infrared type. That this result is to be expected follows from the fact that for radiation of this type Planck's expression reduces to that of Wien, on which Einstein founded his law. So far as experimental data are available Einstein's law (for short waves) has been approximately verified in the case of gaseous reactions (compare Bodenstein, *Zeitsch. physikal. Chem.*, 1913, **85**, 329), but apparently breaks down for photochemical short-wave reactions in the liquid state according to the results obtained by Henri and Würmser (*J. Physique*, 1913, [v], **3**, 305). Baly (*Physikal. Zeitsch.*, 1913,

14, 893) has offered a qualitative explanation of the discrepancy, as due to a contribution of energy made by the solvent which is not considered in Einstein's original treatment. It is of importance to point out that the infra-red radiation hypothesis applied to thermal reactions predicts a modification of the temperature-coefficient when a catalyst is present, that is, the solvent as a particular case. If the catalyst is a positive one, energy less than one quantum is sufficient to energise a molecule; if the catalyst is negative, energy greater than one quantum is apparently required. The effect is, however, very much smaller in magnitude than that observed by Henri and Würmser.

Unimolecular Reaction-velocity in a Gaseous System in the Presence of a Positive Catalyst.

In the case of a reaction, which does not proceed at a measurable speed in the absence of a catalyst, the conclusion drawn from the radiation hypothesis is that the natural radiation density, due to the temperature of the material system, is insufficient to activate a sensible number of molecules per second. The rate can be increased by increasing the radiation density, and this can be brought about in two ways, namely, by the addition of catalyst or by an increase in temperature. In all cases, when speaking of a catalyst in this connexion, homogeneous catalysis, in the first instance, is intended. Catalytic effects, produced by the walls of the vessel, are assumed to be excluded. When a catalyst is present the active mass has been defined as proportional to the concentration of the reactant, multiplied by the concentration of the catalyst, C_s, multiplied by the effective radiation density u_ν. The catalyst is considered as giving rise to the necessary radiation density, and since the concentration of the catalyst remains unchanged throughout the course of the reaction, u_ν will likewise remain constant. Using the same notation as before, the rate of this type of reaction may be written:

$$dx/dt = P(a-x)C_s \,.\, n^3 \,.\, e^{-h\nu/kT} \quad . \quad . \quad . \quad . \quad (8)$$

which at constant temperature reduces to the usual expression for a simple catalytic process, the rate being proportional to the concentration of the reactant and that of the catalyst. On integration we obtain:

$$\frac{1}{t}\frac{\log a}{a-x} = k_{\text{obs.}} = P \,.\, C_s \,.\, n^3 \,.\, e^{-h\nu/kT} \quad . \quad . \quad . \quad (8a)$$

On differentiating with respect to temperature we obtain:

$$\frac{d\log k_{\text{obs.}}}{dT} = \frac{h\nu}{kT^2} = Nh\nu/RT^2 \quad . \quad . \quad . \quad . \quad (9)$$

which is identical with equation (5). That is, the temperature-coefficient is not sensibly affected by the presence of the catalyst in this case. The assumption involved in equation (9) is that the refractive index is independent of temperature. For gaseous reactions, as already pointed out, n is almost unity, and hence the assumption is approximately true. For reactions in solution, n (which is mainly determined by the solvent) is not unity, and is known to vary slightly with the temperature. In the latter case, therefore, equation (9) is no longer exact. It will be shown later that the presence of a positive catalyst diminishes the temperature-coefficient, a negative catalyst increases it, and this conclusion is borne out by experiment.

Influence of the Solvent on the Reaction-velocity (in the Absence of "Added" Catalyst).

It is well known that the solvent is capable of modifying the rate of a reaction to a marked degree. The effect is usually regarded as a catalytic one, and will be treated as such. The system considered is a dilute solution of a reacting substance, in which the main physical properties of the system, such as the dielectric constant and refractive index, are almost entirely determined by the constituent present in excess, namely, the solvent. Treating this type of reaction in the same way as that of a catalysed gas reaction, the velocity should be determined by the concentration of the reactant, the concentration of the catalyst (the solvent), and by the radiation density u_ν of the frequency ν. On the radiation view, therefore, the function of the solvent is to increase the reactivity of the solute by the transfer of quanta of the absorbable type ($h\nu$) to the solute. It is to be anticipated that each solvent would exert a specific effect, owing to differences in chemical constitution, and therefore in radiation distribution. Further, the radiation density depends on the cube of the refractive index n, which, for long waves, is known to be approximately proportional to the square-root of the dielectric constant, which in turn is known to be connected with the observed reaction-velocities. Denoting the concentration of the solvent by C_s, the previous equations, (8) and (8a), apply directly. If we further assume that n is independent of temperature, equation (8a) leads necessarily to equation (9), which, as we have seen, involves—when combined with the Marcelin-Rice relation—the validity of Einstein's law of the photochemical equivalent. The assumption that n is almost independent of temperature can be made for gaseous systems, but not for reactions in solution until we know to what extent n varies with T. This point must now be considered.

The symbol n refers to the wave-length region in the neighbourhood of an infra-red band. On the simple electromagnetic theory the value of n is infinite on the long wave side of the band. On the Lorentz modification of the theory of absorption, however, n is finite,* and may not even be very large. That infinite values are not reached has been shown experimentally for the visible region and later for the ultraviolet. Thus Pflüger (*Ann. Phys. Chem.*, 1895, [iii], **56**, 412) found in the case of certain dyestuffs, in the solid state, that the maximum value of n did not exceed 2·5, the minimum value (reached just on the shorter side of the band) being not less than 0·83.† On the longer wave side the band makes its presence felt in enhanced values of n over a considerable range (50 to 100 $\mu\mu$), the maximum value of n being attained in many cases just at the longer side of the band, or even slightly inside the band. Probably the most accurate determination of n near and through a band is that of Wood (*Phil. Mag.*, 1904, [vi], **8**, 293), in the case of sodium vapour, who found $n_{max.} = 1{\cdot}386$, and $n_{min.} = 0{\cdot}614$. Wood (*ibid.*, 1903, [vi], **6**, 96) also found, in the case of *p*-nitrosodimethylaniline, that n reached its maximum value, 2·30, at $\lambda = 480\ \mu\mu$, just at the long wave side of the band, and its minimum value, 1·05, at the short wave side, $\lambda = 370\ \mu\mu$. The value of n falls steadily through the band from the long to the shorter wave side. Wood and Magnusson (*Phil. Mag.*, 1901, [vi], **1**, 36, 624) determined n from $\lambda = 770\ \mu\mu$ to $370\ \mu\mu$ for cyanine, which shows two marked bands, one in the yellow, the other in the ultraviolet. In the yellow region $n_{max.} = 2{\cdot}35$ at $\lambda = 640\ \mu\mu$, and $n_{min.} = 1{\cdot}12$ at $\lambda = 540\ \mu\mu$. Reference may also be made to measurements of n in the infra-red (although not close to a band) carried out by Nichols (*Ann. Phys. Chem.*, 1897, [iii], **60**, 414), Rubens and Aschkinass (*ibid.*, 1899, [iii], **67**, 459), Rubens and Hollnagel (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 26), and Rubens (*ibid.*, 1913, 513).

As regards the effect of temperature on the refractive index, Sieben (*Ann. Phys. Chem.*, 1884, [iii], **23**, 312) found for solutions of certain dyestuffs that the value of n, measured at some distance from the band which occurs in the visible region, diminishes slowly with rise in temperature according to a linear relation, $n = n_0 - bt$, where b is small. Measurements of this kind have been carried

* The distinction is made clear on comparing, for example, the expressions for the dielectric constant given on pages 37 and 51 respectively, in N. Campbell's "Modern Electrical Theory," second edition

† Cartmel (*Phil. Mag.*, 1903, [vi], **6**, 213) has extended Pflüger's measurements on solid magenta. With a plate thickness of 0·192 μ, Cartmel found that the band extended from 420 $\mu\mu$ to 660 $\mu\mu$, and $n_{max.} = 2{\cdot}7$ at $\lambda = 600\ \mu\mu$, whilst $n_{min.} = 0{\cdot}8$ at $\lambda = 460\ \mu\mu$.

out by E. Liebreich for the infra-red region in the case of rock salt, potassium chloride, and fluorite (*Ber. Deut. physikal. Ges.*, 1911, **13**, i, 700) from room temperature to 60° approximately. The values of n refer to the wave-length 9 μ. In general, for the substances mentioned, the value of dn/dT is two units in the fifth place of decimals of the value of n itself, the index diminishing as the temperature rises. For liquids (measured in the visible region) dn/dT is 10 to 30 times greater than the value quoted. Since, in the present case, n possesses an enhanced value, corresponding with the lower side of a band, dn/dT is also enhanced, for, as will be pointed out later, the greater the absolute value of n the greater is the temperature-coefficient. dn/dT may, therefore, be of the order 0·001 for liquid systems. Even this value shows that n varies only slowly with temperature. So far as measurements have gone, it has been found that a linear relation connects n and T, namely, $n = n_0 - bT$. We shall make use of this relation in the present instance, although it is obviously limited in applicability, for at high temperatures n does not fall below unity.

Allowing for the variation of n with T, and therefore for the effect of the solvent on the temperature-coefficient of the reaction-velocity, the expression for the rate of the reaction (equation 8) takes the following form, where C_s stands for the concentration of the catalysing solvent:

$$dx/dt = P(a-x)C_s n^3{}_0.(1-bT/n_0)^3.e^{-h\nu/kT} = k_0(1-bT/n_0)^3.e^{-h\nu/kT} \quad . \quad . \quad (10)$$

where k_0 is a constant independent of the temperature. It follows, therefore, that

$$k_{obs.} = k_0(1-bT/n_0)^3.e^{-h\nu/kT},$$

Hence,

$$d\log k_{obs.}/dT = Nh\nu/RT^2 - 3b/n_0 - 3b^2T/n_0{}^2,$$

Or,

$$d\log k_{obs.}/dT = Nh\nu/RT^2 - 3\beta - 3\beta^2T = \frac{Nh\nu - 3\beta RT^2 - 3\beta^2RT^3}{RT^2},$$

where $\beta = b/n_0$. Neglecting the term containing the small quantity β^2, we obtain:

$$\frac{d\log k_{obs.}}{dT} = \frac{Nh\nu - 3\beta RT^2}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Equation (11) differs from equation (9) in that the numerator is diminished by a quantity which at low temperatures is small. Equation (11) allows for the presence of a single solvent functioning as a positive catalyst, but does not allow for the effect of an added catalyst, such as another solute or a second solvent mixed with the first, which will be considered in the next section. It will

be observed that the presence of the solvent, indicated by the term β, has caused the Einstein principle to break down, in that the requisite amount of energy reckoned per molecule is no longer $h\nu$, but $h\nu - 3\beta kT^2$. Since k and β are both small, it is doubtful whether equation (11) could be distinguished experimentally from equation (9). For this reason an equation of the Arrhenius type should apply, and does apply, to reactions in solution. As the temperature is raised, however, the numerator ($Nh\nu - 3\beta RT^2$) should diminish. The data so far obtained are not sufficiently accurate, and have not been examined over a sufficiently wide temperature range, to determine with certainty whether this numerator is independent of temperature or not (compare Cain and Nicoll, T., 1903, **83**, 470).

The Effect on the Temperature-coefficient of Altering the Concentration of the Catalyst in Solutions.

In the preceding section the case was considered in which a single solvent functioned as the catalyst. Under these conditions it is impossible to alter the concentration of the catalyst at will. It is of importance, therefore, to consider a reaction proceeding in a solution in which the concentration of the catalyst can be altered, and thereby introduce a change in n. That is, the refractive index has to be expressed as a function of concentration as well as of temperature. The catalyst may be an added solute, such as hydrochloric acid, or a second liquid solvent, the system now consisting of two mixed solvents. As regards the variation of n with concentration, Fricke (*Ann. Physik.*, 1905, [iv], **16**, 865) has shown in the case of certain dissolved dyestuffs, examined in the ultraviolet region, that $n_{max.}$, on the lower side of the band, is increased by an increase in concentration of the solute, whilst $n_{min.}$, at the upper side of the band, is in many cases diminished by an increase in concentration. No measurements have yet been carried out with sufficient exactness to determine the relationship. The effect of concentration in the case of dissolved salts in the visible region is exceedingly small. Thus Schütt (*Zeitsch. physikal. Chem.*, 1890, **5**, 349) has found that, when measured for the potassium red line, the refractive index of an aqueous solution containing 1 per cent. of sodium chloride is 1·331073, whilst for a solution containing 20 per cent. of salt the value is 1·364120; that is an increase of less than 3 per cent. in n for a twenty-fold increase in concentration. In the case of mixed liquids the variation of n with concentration will be greater than in the case of the solutions examined by Schütt. One liquid must act in general as a negative catalyst with respect to the other. For the sake of simplicity we shall

regard one of the liquids as inert, such as appears to be the case for acetone in the inversion of sucrose in acetone–water mixtures (compare Rosanoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1911).

The expression which requires modification is $n = n_0 - bT$. In the first place, an increase in the concentration of the positive catalyst causes n_0 to increase to n_1,* a quantity which is independent of temperature, but depends on the concentration of the catalyst. At the same time the enhanced values of n may possess a different temperature-coefficient from that possessed by a lower value of n. That is, b itself may be a function of the concentration of the catalyst. The following table shows that, in general, the greater the value of n the greater is the temperature-coefficient, that is, the greater is the value of b.

Substance.	Refractive index at 313 abs.	n_0.	b.
Carbon disulphide	$n_D = 1{\cdot}61156$	1·879	0·00049
Dimethylaniline	$n_D = 1{\cdot}54809$	1·712	0·00032
Nitrobenzene	$n_D = 1{\cdot}54212$	1·710	0·00033
Benzonitrile	$n_D = 1{\cdot}51597$	1·654	0·00028
Ethyl alcohol	$n_{(H\alpha)} = 1{\cdot}35154$	1·472	0·00027
Aluminium bromide (11·77 per cent.) in aqueous solution.....	$n_D = 1{\cdot}34412$	1·391	0·00011
Water	$n_{(H\alpha)} = 1{\cdot}32943$	1·362	0·00008

Applying the conclusion drawn from the above table to the case in which n is enhanced by addition of a catalyst, it follows that the temperature-coefficient of n is a function of the concentration, C_s, of the catalyst, in the sense that the enhanced value of n diminishes more rapidly with rise in temperature than does the unenhanced value. That is, in place of b we must employ a slightly more complex quantity, indicating that the value of b increases as C_s increases. The simplest form is to write in place of b the term $(b + \gamma C_s)$, where γ is a small positive quantity. When there is no added catalyst or second liquid present, the coefficient is determined by b as before. It follows from the above that

$$n = n_1\left(1 - \frac{(b + \gamma C_s)T}{n_1}\right).$$

On substituting this expression in equation (10) we obtain for the rate of the reaction:

$$dx/dt = P(a - x)C_s \cdot n_1^3\left(1 - \frac{(b + \gamma C_s)T}{n_1}\right)^3 e^{-h\nu/kT}.$$

Or,

$$dx/dt = k_0(a - x)\left(1 - \frac{(b + \gamma C_s)T}{n_1}\right)^3 e^{-h\nu/kT} \quad . \quad . \quad (12)$$

* The term n_1 could be written as $n_0 + \delta C_s$, where δ is a small positive coefficient.

Whence,

$$k_{obs.} = k_0\left(1 - \frac{(b+\gamma C_s)T}{n_1}\right)^3 e^{-h\nu/kT}.$$

On taking logs. and differentiating with respect to temperature we obtain:

$$d\log k_{obs.}/dT = N h\nu/RT^2 - \frac{3(b+\gamma C_s)}{n_1} - \frac{3(b+\gamma C_s)^2 T}{n_1^2}.$$

Or, again neglecting the term containing b^2,

$$d\log k_{obs.}/dT = \frac{N h\nu - \frac{3(b+\gamma C_s)RT^2}{n_1}}{RT^2} \quad . \quad . \quad . \quad . \quad (13)$$

When the only catalyst present is the single solvent, n_1 becomes n_0, $\gamma C_s = 0$, and the expression reduces to equation (11). It will be seen from the table already given that the temperature-coefficient of n varies much more from substance to substance than does the corresponding value of n_0. That is, in general, $3(b+\gamma C_s)/n_1$ is numerically greater than $3b/n_0$. Hence the numerator of equation (13) is less than the numerator of equation (11); in other words, the presence of the positive catalyst diminishes the temperature-coefficient of the reaction-velocity constant. If the added catalyst be a negative one, the sign before γ must be reversed.* That is, the presence of a negative catalyst increases the value of the temperature-coefficient of the velocity-constant. These conclusions may be stated thus: Any agency which increases the reaction-velocity (positive catalysis) diminishes the temperature-coefficient of the constant; any agency which diminishes the velocity (negative catalysis) increases the value of the coefficient. This statement is borne out by experiment. Thus von Halban (*Zeitsch. physikal. Chem.*, 1909, **67**, 139) has measured the rate of decomposition of triethylsulphine bromide in acetone–water mixtures, and the following table contains the data obtained for the velocity-constants and temperature-coefficients, as well as the numerator of equation (13) calculated by applying the ordinary Arrhenius expression to von Halban's data, that is, $d\log k_{obs.}/dT = E/RT^2$:

Water present in per cent.	Velocity-constant at 60°·($k_{60°}$).	Velocity-constant at 80° ($k_{80°}$).	Ratio $k_{80°}/k_{60°}$.	E in calories per gram-mol.
0·0	0·0077	0·0967	12·6	29720
4·03	0·00060	0·00855	14 3	31320
10·0	0·000044	0·000683	15·5	32240

* The numerator of equation (13) would then be written:

$$N h\nu - \frac{3(b-\gamma C_s)RT^2}{n_0 - \delta C_s}$$

when δ is a smaller coefficient than γ.

In this case acetone acts either as an inert liquid or as a positive catalyst, water as the negative catalyst, and it will be observed that the temperature-coefficient rises as the mean velocity falls. Similar results have been obtained in the decomposition of oxalic acid in sulphuric acid–water mixtures (Bredig and Lichty, *Zeitsch. Elektrochem.*, 1906, **12**, 459; *J. physical Chem.*, 1907, **11**, 225) and in the transformation of acetophenoneoxime to acetanilide in sulphuric acid–water mixtures (de Bruyn and Sluiter, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **6**, 773). In these cases water acts as a negative catalyst with respect to the other solvent. Other illustrations have been referred to in Part II. of this series.

As already stated, equation (13) refers to the case in which one constituent in inert, the other a positive catalyst. In the more general case, one constituent is positive, and the other negative. Equation (13) has therefore to include an additional term analogous to γ, but of opposite sign.*

The relation between the magnitude of the temperature-coefficient and that of the velocity-constant, as modified by the catalysing agency, is also borne out by the results recently obtained by Francis, Geake, and Roche (T., 1915, **107**, 1658) on the decomposition of nitrosotriacetonamine. In aqueous solution the velocity is greater than in alcoholic solution, and corresponding with this the temperature-coefficient (between 30° and 40°) is smaller in the former case than in the latter, namely, in aqueous solution, $k_{40}/k_{30}=2{\cdot}35$; in alcoholic solution, $k_{40}/k_{30}=3{\cdot}0$. This effect of the catalysing agency is also in agreement with the Marcelin-Rice treatment of the problem (compare Rice, *loc. cit.*).

After the relation referred to had been worked out on the basis of the radiation hypothesis it was found that a similar conclusion had been reached previously by A. Skrabal (*Chem. Zeit.*, 1913, **37**, 1169; *Monatsh.*, 1914, **35**, 1157) based on results obtained in the complex series of reactions which occur in the interaction of iodine and alkali. Skrabal states that rapid exothermic reactions possess a small temperature-coefficient, slow endothermic reactions a large coefficient. The contrast between exothermic and endothermic reactions is also to be anticipated on the radiation hypothesis, as will be shown in a later paper. Skrabal, however, has stated the conclusion in a more general manner than can be done at present on the basis of the radiation hypothesis, which deals with the effect

* In a paper by Barendrecht (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 2) the catalytic effect of enzyme on sugar is ascribed to radiation from the enzyme. The nature of the radiation is not in any way specified, so that it is difficult to draw a comparison between the hypothesis suggested by him and that worked out in this paper.

of a different radiational environment on a given reaction or on the two opposed reaction-velocities in a reversible reaction.

As already pointed out in Part II. of this series, the most comparable conditions for examining two velocity-constants different in nature occur in the case of a reversible reaction. If the velocity-constants of the direct and reverse reaction are of the same order of magnitude, the equilibrium point will correspond with the simultaneous presence of reactants and resultants in comparable quantities, such as is found, for example, in the hydrolysis of ethyl acetate when stoicheiometric quantities are employed. Further, from the conclusion already arrived at regarding velocity-constant and temperature-coefficient, we would expect, if the direct and reverse velocity-constants are of the same order of magnitude, that their coefficients would likewise be approximately the same. The equilibrium constant is, however, the ratio of the velocity-constants, and therefore in this case the equilibrium-constant should be almost independent of temperature. This is known to be a fact in the hydrolysis of ethyl acetate. Again, if the "reverse" velocity is much greater than the "direct" velocity, the temperature-coefficients must be greatly different, and therefore the equilibrium-constant should vary much with temperature, and, further, the direction of the change should be that which corresponds with an increase in the equilibrium amount of the species, very little of which exists at the lower temperature. This conclusion is borne out, both as regards magnitude and direction, by the electrolytic dissociation of water, for example. Other problems relating to equilibrium, especially the heat of reaction, will be considered in a later paper.

Summary.

Assuming the validity of two hypotheses, (1) that a substance reacts when its internal energy reaches a critical value, a view put forward by Marcelin and rendered exact by Rice, and (2) that the extra amount of energy required to bring a molecule into the critical condition is communicated by means of infra-red radiation in terms of quanta, absorbed by the substance, it is shown that expressions may be derived for the velocity of ordinary thermal reactions proceeding in the absence and in the presence of a catalyst, which expressions involve the density of the absorbable or useful type of radiation. This term involves the temperature and characteristic frequency of the radiation absorbed by the substance. Under the condition that the temperature is maintained constant, the expressions referred to reduce to the ordinary velocity equations based on the principle of mass action.

Expressions are also obtained for the temperature-coefficients of

the velocity-constants (a) when no catalyst is present, and (b) when either a positive or a negative catalyst is present. These expressions are all in agreement for small intervals of temperature with the empirical equation of Arrhenius, which is known to be generally applicable. It is possible, further, to show how the magnitude of the temperature-coefficient depends on the presence of the catalyst, the most important conclusion being that addition of a negative catalyst raises the temperature-coefficient, whilst a positive catalyst diminishes it. This conclusion has been verified experimentally in the few cases so far available. In the same connexion the applicability of Einstein's law of the photochemical equivalent is shown to be limited (as an exact expression) to those cases in which the refractive index of the system for the absorbable radiation is approximately unity, that is, in the case of gaseous reactions. When a solvent or other catalyst is present, effects enter which are not taken account of in the ordinary statement of Einstein's law.

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LXXI.—*Cryptopine and Protopine.*

By WILLIAM HENRY PERKIN, jun.

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*epi*Cryptopine (*B*) and its Salts, Acetyl Derivative, Conversion of *epi*Cryptopine (*B*) into (*A*) 1011

*epi*Cryptopine (*C*), Acetate, Acetyl Derivative 1012

The *epi*Cryptopirubin Salts 1014

*epi*Cryptopirubin Chloride, Iodide, Dehydro*epi*cryptopirubin Hydroxide, Keto*isoepi*cryptopirubin Hydrochloride, and Hydroxide . . . 1015

The *epi*Methylcryptopines (*A*) and (*B*) 1019

*isoepi*Methylcryptopine 1022

Section XI.

Protopine 1023

*iso*Protopine Chloride and Disulphate 1023

Anhydroprotopine 1024

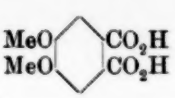
Protopine Methosulphate and the Methylprotopines (α) and (γ) . . 1027

Section I.

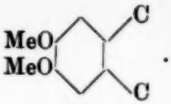
Introduction.

The alkaloid cryptopine occurs in opium, and was discovered in 1867 by J. Smiles in the works of T. and H. Smith, of Edinburgh, in the filtrate after the morphine had been separated, and from which the thebaine had been removed in the form of the tartrate (*Pharm. J.*, [ii], **8**, 595).

Shortly afterwards, Cook (*loc. cit.*, p. 716) analysed the base, and assigned to it the composition $C_{23}H_{25}O_5N$, but the preparations examined were not quite pure, and were subsequently shown to have contained traces of thebaine. The difficulty experienced in obtaining cryptopine quite pure was mainly due to the fact that opium contains such very small quantities of this alkaloid, and T. and H. Smith state indeed that they were able to isolate only 5 ounces of the hydrochloride from 10,000 lbs. of opium. In 1872 Hesse (*Annalen*, *Suppl.*, **8**, 300) described a method for preparing cryptopine free from thebaine and protopine, and succeeded in obtaining 80 grams of this valuable alkaloid in a pure state; he observed the correct melting point (217°), and, as the result of several closely agreeing analyses, assigned to it the correct formula, $C_{21}H_{23}O_5N$. Hesse also prepared and analysed a considerable number of the salts of cryptopine, and obtained nitrocryptopine, $C_{21}H_{22}(NO_2)O_5N$ (compare p. 894), from cryptopine by the action of dilute nitric acid. In a subsequent communication (*Annalen*, 1874, **176**, 200) Hesse added the important observation that cryptopine itself, and also its hydrochloride, are inactive, and in the present communication (p. 881) this statement is confirmed, and it is shown that the alkaloid is not only inactive, but that it is also incapable of resolution by the fractional crystallisation of its tartrate or bromocamphorsulphonate. The physiological action of cryptopine has been investigated by J. Munk (*Dissertation*, Berlin, 1873), W. von Schroeder (*Arch. expt. Path. Pharm.*, 1883, **17**, 140), and Zutz (*Arch. expt. Path. Pharm.*, 1897, **38**, 408). It produces increased reflex excitability and tremulous movements in the cat and rabbit, convulsions with large doses, and causes death by paralysis of the respiratory centre. It paralyses the central nervous system in the frog. The first clue to the constitution of cryptopine was obtained by D. Rainy Brown and W. H. Perkin, jun., in 1891 (P., **7**, 166), who, after confirming the formula, $C_{21}H_{23}O_5N$, assigned to this alkaloid by Hesse, showed that it contains two methoxy-groups, and yields *m*-hemipinic acid (I) when it is oxidised by permanganate (compare p. 889), a result which shows that cryptopine must contain the grouping (II):

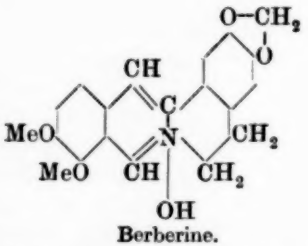


(I.)

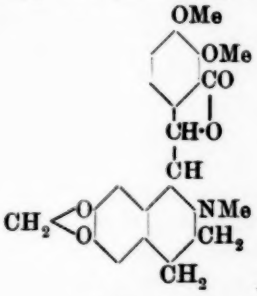


(II.)

It is certainly remarkable that, although the alkaloid has been the subject of repeated investigation more particularly during recent years, *m*-hemipinic acid remains, to the present day, the only degradation product which has been obtained, and there is no direct evidence as to the nature of that part of the cryptopine molecule which does not yield *m*-hemipinic acid on oxidation. Indirect evidence as to the nature of the other section of the alkaloid may, of course, be readily deduced from a comparison of its composition with those of such alkaloids as berberine, $C_{20}H_{19}O_5N$, and hydrastine, $C_{21}H_{21}O_6N$, both of which contain only two methoxy-groups,



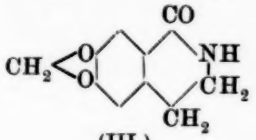
Berberine.



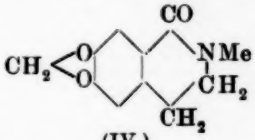
Hydrastine.

and the conclusion becomes irresistible that cryptopine, $C_{21}H_{23}O_5N$, also most probably contains a second benzene nucleus to which the methylenedioxy-group is attached. This conclusion is supported by the observation of Pictet and Kramers (*Ber.*, 1910, **43**, 132) that cryptopine shows certain reactions which are stated to be characteristic of the methylenedioxy-group, and are probably in reality due to the elimination of formaldehyde under the conditions of experiment. Thus the deep violet solution of cryptopine in sulphuric acid is first decolorised and then becomes green on the addition of a 5 per cent. solution of gallic acid in alcohol (Labat, *Bull. Soc. chim.*, 1909, [iv], **5**, 745), again the solution in sulphuric acid gives with phloroglucinol a red coloration and, on heating on the water-wath, a red precipitate (Gaebel, *Arch. Pharm.*, 1910, **248**, 225). No direct evidence of the presence of the methylenedioxy-group in the alkaloid had, however, been obtained, and one of the most perplexing problems in connexion with the present investigation has been the difficulty of devising some reaction which would lead to the isolation of substances derived from the methylenedioxybenzene or piperonyl group in cryptopine.

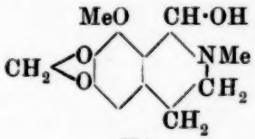
In order to accomplish this, the alkaloid was subjected to the action of a long series of oxidising and hydrolytic agents under a great variety of conditions, but in every case the piperonyl ring was completely destroyed and the only substances that could be isolated were derived from the dimethoxybenzene nucleus. This is the more remarkable when it is remembered that all the other alkaloids which contain the piperonyl group exhibit an entirely different behaviour. Thus berberine readily yields 6:7-methylenedioxytetrahydro*iso*quinolone (ω-aminoethylpiperonylcarboxylic anhydride) (III), hydrastine yields oxyhydrastinine (IV), and narcotine yields cotarnine (V) when subjected to the action of suitable oxidising



(III.)



(IV.)



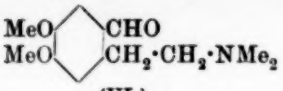
(V.)

agents, substances which all contain the piperonyl group. This difficulty has only comparatively recently been overcome, and the isolation of piperonyl derivatives from cryptopine was ultimately accomplished by making use of a reaction which does not appear to have been previously employed, and may have wide applicability in the future. Cryptopine combines readily with methyl sulphate, yielding the methosulphate, $C_{21}H_{23}O_5N,Me_2SO_4$ (p. 880), and when this is reduced in boiling acid solution with sodium amalgam, a curious process takes place and *tetrahydromethylcryptopine*, $C_{22}H_{29}O_5N$ (m. p. 107°, p. 896), is produced. Acetyl chloride reacts readily with this substance, water is eliminated, and the result is the formation of *anhydrotetrahydromethylcryptopine*, $C_{22}H_{27}O_4N$, which also melts at 107°. When this substance is oxidised by dry potassium permanganate in acetone solution, it yields a syrupy base, *A* (b. p. 190°/10 mm.), an aldehyde, *B* (m. p. 74—75°), an acid, *C* (m. p. 153°), an acid, *D* (m. p. 217°), and *m*-hemipinic acid. The syrupy base, *A*, has the empirical formula $C_{13}H_{19}O_3N$, contains two methoxy-groups, and is converted by treatment with methyl iodide into the methiodide, $C_{13}H_{19}O_3N,MeI$, which melts at 203° and yields a characteristic oxime,

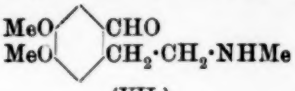
$$C_{12}H_{19}O_2N(C{:}N{\cdot}OH),MeI$$

(m. p. 223°). These facts seemed to suggest that the syrupy base, *A*, is in all probability the methyl derivative (VI) of 4:5-dimethoxy-

2-β-methylaminoethylbenzaldehyde (VII), which Pyman (T., 1909,



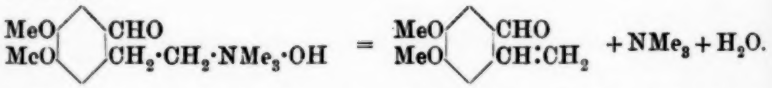
(VI.)



(VII.)

95, 1272) first prepared from laudanosine by oxidation with manganese dioxide and sulphuric acid. In order to test this supposition, the substance (VII) was treated with methyl iodide, when it yielded the hydriodide of the base, $R{\cdot}CH_2{\cdot}CH_2{\cdot}NHMe,HI$ (i), the hydriodide of the methyl base, $R{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,HI$ (ii), and the methiodide, $R{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$ (iii). These were separated by fractional crystallisation, and (iii) was found to melt at 203° and to be identical with the methiodide obtained from base *A* by the action of methyl iodide; moreover, (ii) yielded on treatment with alkali a syrupy base which distilled at 190—193°/11 mm., and was identical with the syrupy base *A*. It is therefore clear that this base is 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde, and has the constitution represented by formula VI.

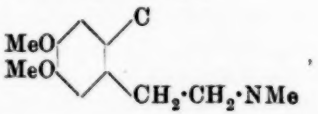
An interesting decomposition of the methiodide of this base is its behaviour with alkalis when it is decomposed with elimination of trimethylamine and formation of 4:5-*dimethoxy-2-vinylbenzaldehyde*:



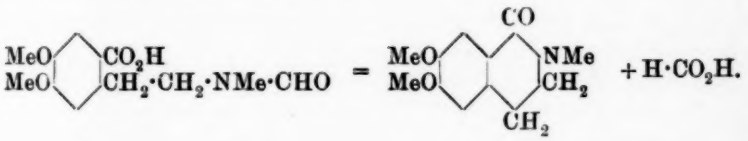
This substance had not previously been described, and is closely allied in constitution and properties to 4:5-methylenedioxy-2-vinylbenzaldehyde (hydrastal, m. p. 79°),

which is similarly obtained by boiling trimethylhydrastylammonium iodide with potassium hydroxide (Freund, *Ber.*, 1889, **22**, 2333). It is a colourless, crystalline substance, melts at 55°, and yields a characteristic oxime (m. p. 126°) and semicarbazone (m. p. 226°).

The formation of 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde (VI) by the oxidation of anhydrotetrahydromethylcryptopine affords valuable evidence as to the constitution of the lower section of the cryptopine molecule, since it shows that the alkaloid must contain the grouping:



and this conclusion receives confirmation from the examination of the acid *C* (m. p. 153°), which is also produced in small quantities during the same decomposition (compare pp. 923 and 925). This curious substance has the formula $C_{13}H_{17}O_5N$, is a monobasic acid, and has at the same time feebly basic properties, since it yields a hydrochloride, $C_{13}H_{17}O_5N,HCl$, and a sulphate, $C_{13}H_{17}O_5N,H_2SO_4$, both of which are crystalline and dissociated by water. It contains two methoxy-groups and belongs, therefore, to the same part of the cryptopine molecule as the syrupy base *A*, but for a long time no other definite information as to its structure could be obtained. Ultimately it was discovered that it is converted by heating with dilute sulphuric acid at 150°, or, better still, by simply heating in the dry state into 6:7-dimethoxy-2-methyltetrahydro*iso*quinolone, a substance first obtained by Pyman (T., 1909, **95**, 1272). Since the elements of formic acid are removed during this decomposition it follows that the acid *C* is *N-formyl-4:5-dimethoxy-2-β-methylaminoethylbenzoic acid*, and the change just mentioned may be represented in a simple manner, thus:



The aldehyde, *B*, and the acid, *D* (p. 824), produced during the oxidation of anhydrotetrahydromethylcryptopine were then examined and found to be free from methoxy-groups, so that they evidently belong to the methylenedioxybenzene portion of the cryptopine molecule, and are the substances which were so long sought for in vain. The aldehyde melts at 74—75°, has the odour of piperonal, and yields a characteristic oxime (m. p. 145°), semicarbazone (decomposing point 248°), and phenylhydrazone (m. p. 106°), and as its formula is $C_9H_8O_3$ it must clearly be a methyl derivative of piperonal and have the formula $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$.

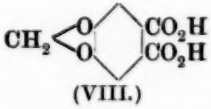
In order to determine the relative positions of the various groups in this aldehyde it was heated with phosphorus pentachloride, followed by treatment with formic acid and boiling water, under the conditions recommended by Barger (T., 1908, **93**, 572) in the corresponding case of piperonal, and thus converted into the substances $CCl_2{:}O_2{:}C_6H_2Me{\cdot}CHO$, $CO{:}O_2{:}C_6H_2Me{\cdot}CHO$ (m. p. 104°), and $(OH)_2C_6H_2Me{\cdot}CHO$ (m. p. 168°). Finally, the dihydroxyaldehyde was methylated by treatment with methyl sulphate in the presence of sodium ethoxide and converted into the corresponding dimethoxyaldehyde, $(MeO)_2C_6H_3{\cdot}CHO$, which melted at 53° and yielded an oxime (m. p. 99°) and a semicarbazone (m. p. 220°). It

was thought possible that this dimethoxyaldehyde might be identical with 4:5-dimethoxy-*o*-tolualdehyde,

which Perkin and Weizmann (T., 1906, **89**, 1650) obtained by the action of anhydrous hydrogen cyanide on dimethylhomocatechol in the presence of aluminium chloride, more particularly as the semicarbazones of the two aldehydes melt at the same temperature. The 4:5-dimethoxyaldehyde, however, melts 23° higher than the aldehyde from cryptopine, and, moreover, a mixture of the two softens at 30°, so that they cannot possibly be identical.

The experimental proof of the exact position of the methyl and aldehydo-groups in this aldehyde, *B*, was found to be a matter of much difficulty, but it was ultimately deduced in the following manner: The aldehyde was first oxidised by permanganate, when it yielded a methylpiperonylic acid, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$, which melted at 216—217°, and proved to be identical with the acid *D*, which had been obtained as one of the products of the oxidation of anhydrotetrahydromethylcryptopine (p. 821).

Attempts were next made to oxidise this acid to the corresponding dibasic acid, $CH_2{:}O_2{:}C_6H_2(CO_2H)_2$, in order to determine whether an *o*-dicarboxylic acid isomeric with hydrastic acid (VIII), and consequently having the formula (IX), would be produced:



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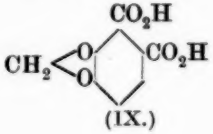


(IX.)

but these were unsuccessful.

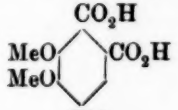
Methylpiperonylic acid is indeed oxidised by permanganate with quite unusual rapidity even at −5°, but in such a way that, whilst part is entirely destroyed, the rest remains unchanged, and this behaviour is in harmony with the experience that it has not been found possible to isolate this acid or any of its derivatives from the product of the permanganate oxidation of cryptopine (p. 821). The next step was to submit the methylpiperonylic acid to the action of phosphorus pentachloride, formic acid, and water, as had already been done in the case of the corresponding aldehyde (p. 823), and this resulted in the formation of the substances

$CCl_2{:}O_2{:}C_6H_2Me{\cdot}COCl$,

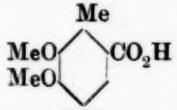
$CO{:}O_2{:}C_6H_2Me{\cdot}CO_2H$, and $(OH)_2C_6H_2Me{\cdot}CO_2H$ (m. p. 202°). When the dihydroxy-acid was methylated in alkaline solution with methyl sulphate it was converted into a new dimethoxymethylbenz-

oic acid, $(MeO)_2C_6H_2Me\cdot CO_2H$ (m. p. 177°), which on oxidation with permanganate was not destroyed as in the case of the corresponding methylenedioxy-acid, but gave a good yield of hemipinic acid (X).

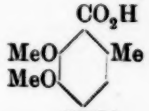
It follows, therefore, that its constitution must be represented by either (XI) or (XII):



(X.)



(XI.)

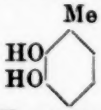


(XII.)

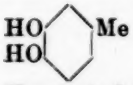
Owing to the very small amount of material available, the decision between these two formulæ was for a long time impossible, but recently it was discovered that the dihydroxy-acid,

$$(OH)_2C_6H_2Me\cdot CO_2H$$

(m. p. 202°), is decomposed by heating with water at 170—180° with elimination of carbon dioxide and formation of a dihydroxytoluene, which was found on careful examination to be *iso*homocatechol, and not homocatechol:

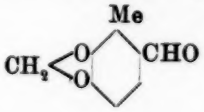


*iso*Homocatechol.

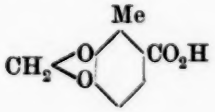


Homocatechol.

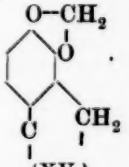
The dimethoxy-acid melting at 177° is therefore 5:6-dimethoxy-*o*-toluic acid (XI), and it follows from this proof that the aldehyde *B* (m. p. 75°) and the acid *D* (m. p. 217°), produced by the oxidation of anhydrotetrahydromethylcryptopine (p. 821), must be 5:6-methylenedioxy-*o*-tolualdehyde (XIII) and 5:6-methylenedioxy-*o*-toluic acid (XIV) respectively, and that the molecule of cryptopine therefore contains the piperonyl ring in its upper section and in the form of the nucleus (XV):



(XIII.)



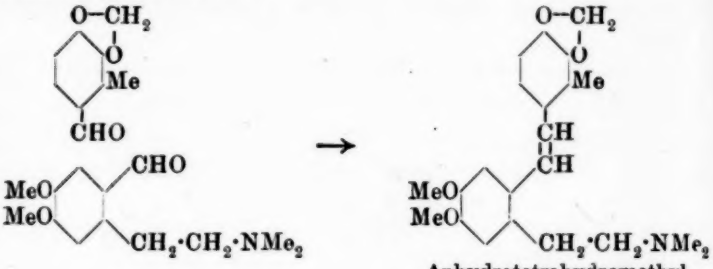
(XIV.)



(XV.)

The constitutional formula for anhydrotetrahydromethylcryptopine may now be built up from the degradation products, 5:6-methylenedioxy-*o*-tolualdehyde and 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde, on the assumption that the two aldehyde groups in these two substances have been produced by the oxidation of an ethylenic linking. The reconstruction of the formula of

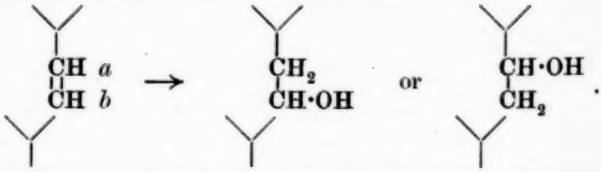
anhydrotetrahydromethylcryptopine may therefore be indicated by the following scheme:



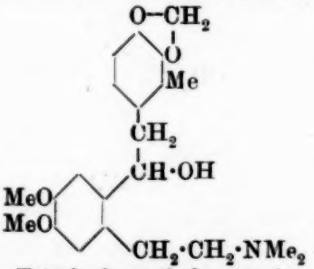
Anhydrotetrahydromethylcryptopine.

This substance is obtained from tetrahydromethylcryptopine by the elimination of water and consequent formation of the ethylenic linking.

It is therefore possible to deduce the formula of the latter by again adding the elements of water to the ethylenic linking, and this process gives rise to two possible formulæ, since the addition can obviously take place in two different ways according to whether the groups are added in the direction *ab* or *ba*:



Definite evidence will be brought forward in later chapters of this research, and in particular in the chapter dealing with the properties of dihydrocryptopine (p. 839), which proves conclusively that the addition of H– and OH– must be made in the direction *ab*, and that the formula of tetrahydromethylcryptopine is therefore:



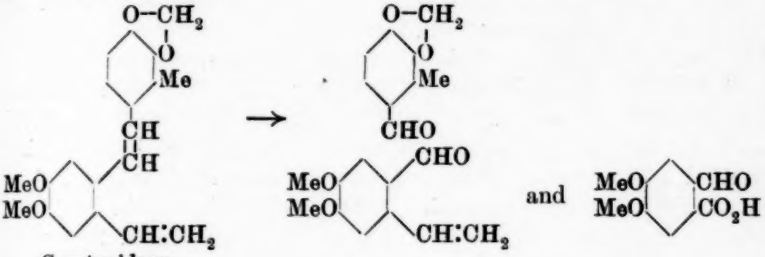
Tetrahydromethylcryptopine.

Interesting results were obtained during the course of experiments which had for their object the elimination of nitrogen from anhydrotetrahydromethylcryptopine. The methosulphate of this

substance is readily prepared by direct addition, and when digested with methyl-alcoholic potassium hydroxide is decomposed with elimination of trimethylamine and formation of a substance, $C_{20}H_{20}O_4$, which melts at 124° and has been named *cryptopidene* (p. 926):

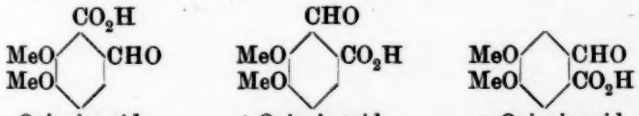
$$C_{22}H_{27}O_4N,Me_2SO_4 + KOH = C_{20}H_{20}O_4 + NMe_3 + KMeSO_4 + H_2O.$$

When this substance is oxidised with permanganate it yields 5:6-methylenedioxy-*o*-tolualdehyde (and 5:6-methylenedioxy-*o*-toluic acid), 4:5-dimethoxy-2-vinylbenzaldehyde, *m*-opianic acid (and *m*-hemipinic acid):



Cryptopidene.

The formula for cryptopidene, deduced in the usual manner from that of anhydrotetrahydromethylcryptopine, is obviously in harmony with the formation of this series of degradation products. The discovery of *m*-opianic acid as one of the products of the oxidation of cryptopidene is particularly interesting because this acid is new and is the last of the opianic acids, and its isolation therefore completes the series of these important acids, all of which have been obtained from alkaloids or their degradation products by processes of oxidation:

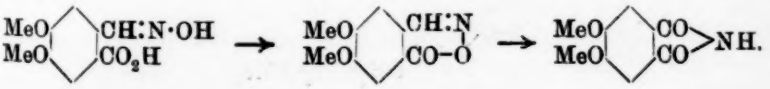


Opianic acid (m. p. 150°) from narcotine.

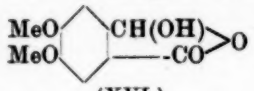
ψ-Opianic acid (m. p. 121°) from berberine.

m-Opianic acid (m. p. 184°) from Cryptopine.

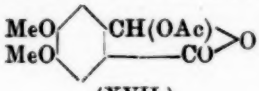
In its properties *m*-opianic acid closely resembles the other members of the group. The semicarbazone (m. p. 227°) is sparingly soluble, and the oxime readily yields an anhydride which, on heating, is converted by the interesting molecular change, which is also characteristic of the oximes of the other opianic acids, into *m*-hemipinimide:



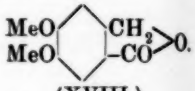
As in the case of the other opianic acids it may react as a hydroxylactone (XVI); thus, for example, when treated with acetic anhydride it yields acetyl-*m*-opianic acid (XVII, m. p. 159°), which is insoluble in alkalis and has other properties in common with ordinary acetylopianic acid (m. p. 121°). It is also readily reduced by sodium amalgam with formation of *m*-meconine (XVIII):



(XVI.)



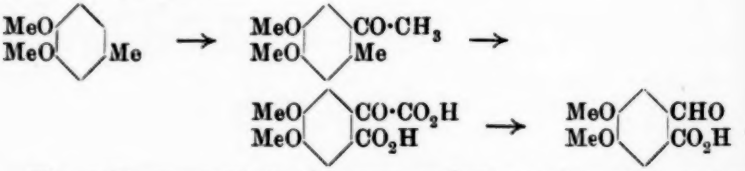
(XVII.)



(XVIII.)

The synthesis of *m*-opianic acid has recently been carried out by the author in conjunction with R. G. Fargher by the following series of reactions, details of which it is hoped will shortly be published.

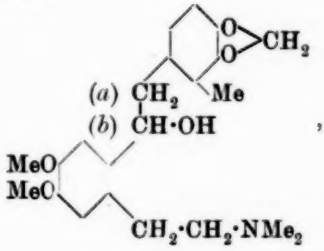
4:5-Dimethoxy-*o*-tolyl methyl ketone, prepared by Harding and Weizmann's method (T., 1910, **97**, 1126) by the action of acetyl chloride in the presence of aluminium chloride on homocatechol methyl ether, was oxidised by permanganate to 6-carboxy-3:4-dimethoxyphenylglyoxylic acid. When this acid is boiled with sodium hydrogen sulphite it undergoes a change similar to that of the conversion of phthalonic acid into phthalaldehydic acid, and yields *m*-opianic acid:



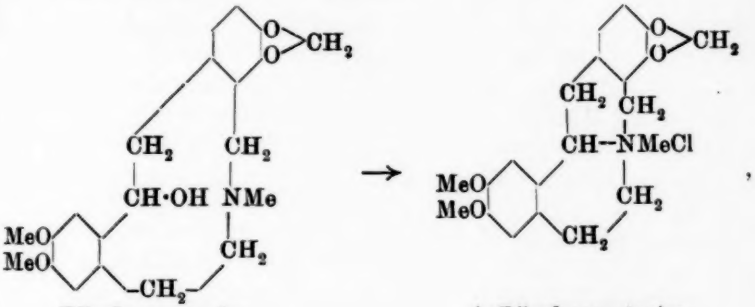
The acid, prepared in this way, melted at 183—184°, and was identical in all its properties with the *m*-opianic acid obtained from cryptopidene by oxidation with permanganate.

The Constitution of Cryptopine.

In the preceding pages the opinion is expressed that tetrahydromethylcryptopine—the substance produced by the reduction of cryptopine methosulphate with sodium amalgam in acid solution—must have the formula:



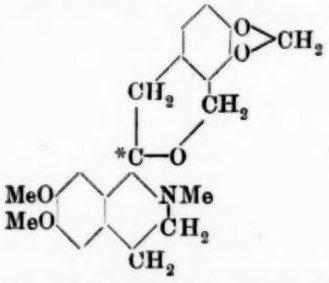
and the only point which at this stage may appear open to doubt is the relative positions of the $>CH_2$ and $>CH\cdot OH$ groups in the centre of the formula, since it is conceivable that these positions might be reversed so as to place the $>CH\cdot OH$ group in the position (*a*). The proof that the position assigned above is correct is an indirect one, and is largely based on the consideration of the formation and properties of the methylcryptopines (p. 847) and on the results of the close comparison of the properties of *iso*dihydrocryptopine chloride with those of tetrahydroberberine methochloride (p. 840). The detailed study of the methylcryptopines has yielded results which, in the opinion of the author, cannot be explained on the assumption that the fifth oxygen atom in cryptopine is attached to (*a*), and the comparison of *iso*dihydrocryptopine chloride with tetrahydroberberine methochloride clearly points to the fact that the formation of the former from dihydrocryptopine must be represented by the scheme:



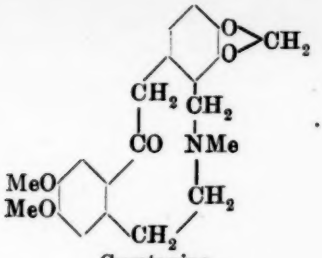
Dihydrocryptopine. *iso*Dihydrocryptopine chloride.

which again necessitates that the fifth oxygen atom in cryptopine must occupy the position (*b*). If, then, this view of the constitutions of tetrahydromethylcryptopine and dihydrocryptopine is accepted, it is possible at once to proceed to the consideration of the constitution of cryptopine itself. In the molecule of cryptopine, $C_{21}H_{23}O_5N$, four of the five oxygen atoms are accounted for by the methylenedioxy- and the two methoxy-groups, and the main difficulty lies in the determination of the nature of the fifth oxygen atom. This oxygen atom exhibits inactive properties to an extraordinary degree. Thus cryptopine does not yield an acetyl derivative, and therefore this oxygen atom is not present in the form of hydroxyl; it also does not combine with hydroxylamine or semicarbazide, and this evidence is therefore against the presence of the carbonyl group. These considerations naturally led, in the earlier stages of this investigation, to the conclusion that the fifth oxygen atom owed its inactivity to the fact that it was present in the

ether or –C·O·C– condition, and that therefore cryptopine probably had the constitutional formula:

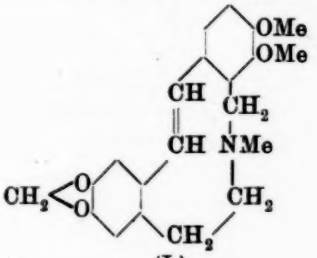


The careful examination of this formula in the light of the changes and decompositions which cryptopine is shown in the following pages to undergo, brings out clearly the remarkable fact that most of these changes and decompositions may indeed be quite readily explained with the aid of this formula. On the other hand, some changes, such as, for example, the formation and properties of the methylcryptopines, are almost impossible to reconcile with this representation. The main argument against this formula is the consideration that it contains an asymmetric carbon atom (*), whereas every specimen of cryptopine which has so far been examined has always been quite inactive. When an alkaloid is capable of existing in active modifications it is very unusual, on extracting it from the plant, to obtain it in its *dl*-modification, and that the inactive modification should appear exclusively, as in the case of cryptopine, has so far not been observed in any case. On the other hand, it might reasonably be urged that the long series of operations, involving as they do the frequent use of acids and alkalis, which are necessary before the minute quantity of cryptopine present in opium can be extracted, are in themselves sufficient to cause complete racemisation of the active alkaloid. This view receives some support from the consideration that gnoscopine (*dl*-narcotine) is found in not inconsiderable quantity in the mother liquors of the preparation of *d*-narcotine from opium. In order to determine whether cryptopine is perhaps the *dl*-modification, the tartrate and the β-bromocamphorsulphonate were prepared and both submitted to extended fractional crystallisations (p. 881), but in no case could any sign of resolution be detected, and the conclusion is therefore justified that cryptopine is incapable of resolution, and must be represented by a formula which demonstrates this peculiarity. So far as can be seen, there is only one formula which satisfies this condition and at the same time offers an adequate explanation of the chemical properties and decompositions of cryptopine, and that is the expression:

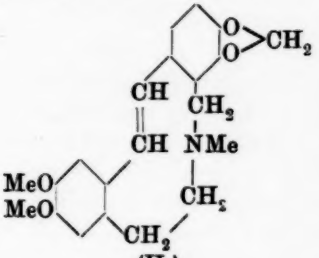


Cryptopine.

Satisfactory as this formula is as a vehicle for the explanation of the known decompositions of cryptopine, there are certain difficulties in the way of immediately accepting it. In the first place, it is unusual, since no alkaloid has, so far, been found to contain the ten-membered ring which is the feature of the above expression. On the other hand, many substances have been obtained during recent years from berberine by Pyman (T., 1913, **103**, 828) and by Freund (*Annalen*, 1913, **397**, 30) in which the ten-membered ring has been found to exist, and special mention may be made of anhydromethyl*iso*tetrahydroberberine (I), and also the fact that a similar substance, called anhydrodihydrocryptopine (II), is obtained from dihydrocryptopine by dehydration (p. 841):



(I.)



(II.)

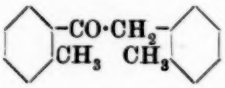
Another objection to the formula for cryptopine given above is that it contains the group $-CO\cdot CH_2-$, and yet cryptopine does not yield an oxime or semicarbazone, nor does it exhibit the reactivity which is usually associated with a $>CH_2$ group in direct combination with the carbonyl group. Cryptopine does not, for example, yield an *iso*nitroso-derivative when treated with *iso*amyl nitrite and sodium ethoxide.

This formula for cryptopine represents the alkaloid as a derivative of deoxybenzoin, $C_6H_5\cdot CO\cdot CH_2\cdot C_6H_5$, which not only yields an oxime (V. Meyer and L. Oelkers, *Ber.*, 1888, **21**, 1298), but is also converted by nitrous acid into *iso*nitrosodeoxybenzoin,

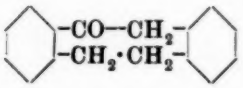
$$C_6H_5\cdot CO\cdot C(:N\cdot OH)\cdot C_6H_5$$

(*ibid.*, p. 1303). The explanation which is offered to account for

this marked difference in properties is that the reactivity of the $-CO\cdot CH_2-$ group in cryptopine is negatived by the steric hindrance exerted by the closing of the ring in the two *o*-positions. In this connexion it would be interesting to prepare and examine the properties of the substances



and



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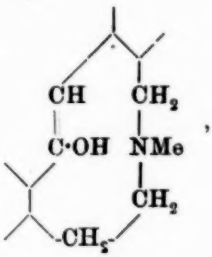
in order to determine the ease with which they yield oximes and *iso*nitroso-derivatives, and experiments with this object in view have been commenced. In discussing the question of the constitution of cryptopine there is a further alternative to be borne in mind, namely, that the alkaloid may exist as the enolic modification containing the grouping:



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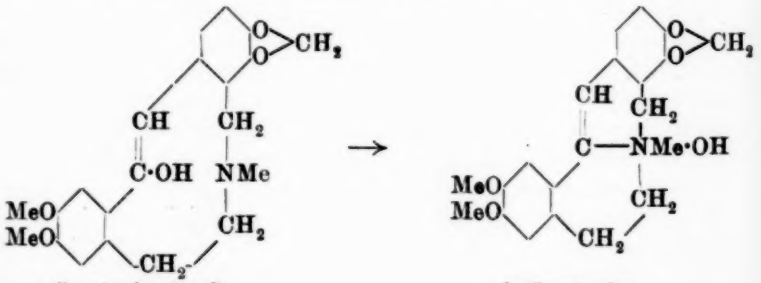
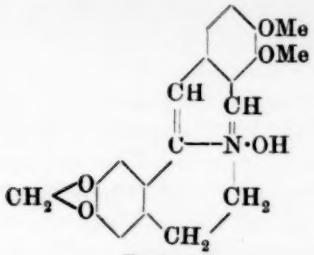
but this is improbable in view of the fact that cryptopine is remarkably resistant to permanganate at the ordinary temperature and does not appear to yield an acetyl derivative.

That cryptopine does frequently react as the enolic modification is quite clear from the consideration of the quaternary *iso*cryptopine salts (see the next section), in the formation of which the hydroxy-group of the enol wanders to the opposite >NMe group, thus:



Cryptopine (enol). *iso*Cryptopine.

It is worthy of note that the structure of *iso*cryptopine is related to that of berberine:

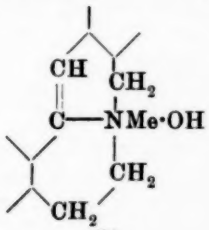


Berberine.

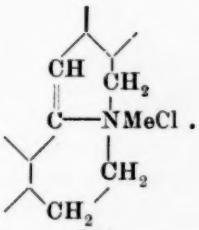
in a very striking manner, and the fact that berberine is highly coloured whereas *iso*cryptopine is almost colourless is well explained by the presence of the conjugated double linking in the centre of the formula of berberine and its absence in the corresponding position in the formula of *iso*cryptopine.

The Quaternary Salts of iso*Cryptopine.*

These important salts are derived from the formula of *iso*cryptopine (I), that is, from the base which is produced when the hydroxyl group of the enolic modification of cryptopine becomes attached to the nitrogen atom and the dihydro*iso*quinoline ring is closed (compare the last section, p. 832):



(I.)



(II.)

The conversion of cryptopine into *iso*cryptopine chloride (II) may be brought about, but not readily, by boiling with hydrochloric acid, better by digesting with acetyl chloride, and the change takes place easily and almost quantitatively when phosphoryl chloride is employed as the reagent. This chloride shows the usual properties of quaternary chlorides, it is sparingly soluble in water, and its aqueous solution does not give a precipitate on the addition of ammonia. On the other hand, when the salt is digested with methyl-alcoholic potassium hydroxide, it is readily decomposed with elimination of hydrogen chloride and formation of *anhydrocryptopine* (p. 850):

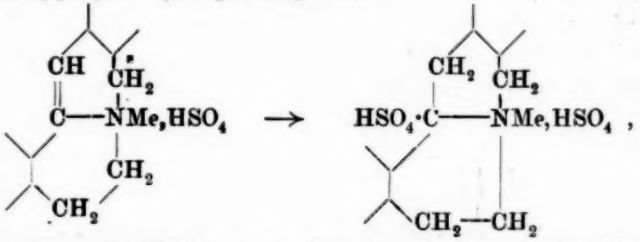
$$C_{21}H_{22}O_4NCl \longrightarrow C_{21}H_{21}O_4N + HCl.$$

Besides this chloride, the *iodide*, $C_{21}H_{22}O_4NI$, the *platinichloride*,

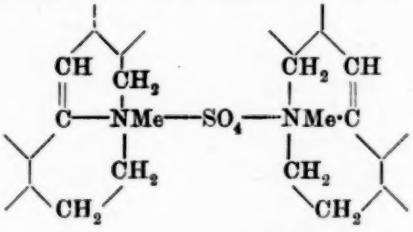
$(C_{21}H_{22}O_4N)_2PtCl_6$, and the *aurichloride*, $(C_{21}H_{22}O_4N)AuCl_4$, have been prepared and analysed (p. 884).

Perhaps the most characteristic and curious salt of *iso*cryptopine is the *disulphate*, which is obtained when cryptopine is digested with glacial acetic acid and concentrated sulphuric acid under the conditions described on p. 884. The very sparingly soluble and beautifully crystalline salt which separates during this process has the composition $C_{21}H_{22}O_4N,HSO_4,H_2SO_4$, and when it is boiled with ammonia it loses sulphuric acid and yields *iso*cryptopine sulphate, $(C_{21}H_{22}O_4N)_2SO_4$, which is also very sparingly soluble. This sulphate exists in well-defined, polymorphous modifications, namely, as a voluminous, satiny mass which is readily soluble in methyl alcohol and as very sparingly soluble, yellow prisms, which gradually develop when the satiny modification is allowed to remain in contact with methyl alcohol.

With regard to the constitution of *iso*cryptopine disulphate there can be little doubt that its formation is due to the addition of sulphuric acid to the double linking contained in the formula of the *iso*cryptopine hydrogen sulphate:



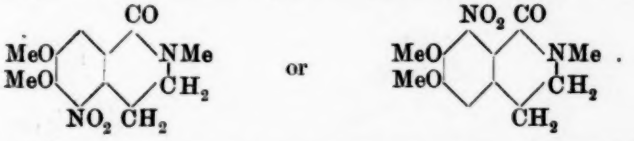
or the H- and -HSO_4 may add on in the reverse direction, and there is reason to suppose that other alkaloids containing a similar double linking may also yield salts of this type under the same conditions. In the conversion of this disulphate into *iso*cryptopine sulphate by the action of ammonia this additive molecule of sulphuric acid, and also a molecule of sulphuric acid from two HSO_4 groups, are removed, and the normal sulphate has, no doubt, the constitution expressed by the partial formula:



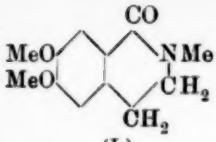
The Action of Nitric Acid on Cryptopine.

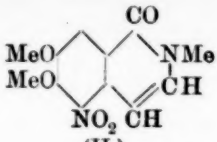
The careful study of the behaviour of the alkaloids when subjected to the oxidising action, more especially of dilute nitric acid, has repeatedly yielded results which have proved to be of great value in developing constitutional formulæ, and this has been particularly prominent in the cases of the alkaloids, hydrastine, narcotine, berberine, and corydaline. There seemed reason to hope that valuable evidence bearing on the constitution of cryptopine might be obtained under similar conditions, and a large number of comparative experiments were therefore instituted on the behaviour of this alkaloid when treated with nitric acid of different strengths and under a variety of conditions, but on the whole the results have been somewhat disappointing. The first to examine the behaviour of cryptopine towards nitric acid was Hesse (*Annalen, Suppl.*, 1872, **8**, 299), who showed that the alkaloid is converted, by the action of very dilute nitric acid (D 1·06) at 60°, into nitrocryptopine, $C_{21}H_{22}(NO_2)O_5N$, which melts at 185° and is characterised by the sparing solubility of its nitrate in dilute nitric acid. During the course of the present investigation the author has repeatedly encountered this substance, and can confirm in every particular the observations carried out so many years ago by Hesse. The main results of the experiments described in the experimental part of the present communication (pp. 890–896) may be briefly summarised as follows: When cryptopine is heated on the steam-bath with dilute nitric acid (D 1·2) it yields a variety of products, some of which are crystalline and some amorphous, and of these the following substances have been isolated and carefully examined:

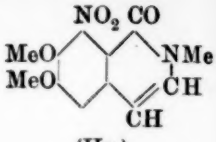
5(or 8)-*Nitro*-6 : 7-*dimethoxy*-2-*methyltetrahydro*isoquinolone,



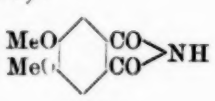
This neutral yellow substance melts at about 245—259°, has very feeble basic properties, and is evidently the nitro-derivative of 6 : 7-dimethoxy-2-methyltetrahydro*iso*quinolone (I) which Pyman (T., 1910, **97**, 269) first prepared. The nitro-derivative has not been described, and is obviously difficult to obtain directly owing to the fact that the above quinolone is so readily oxidised. Thus Pyman showed that when warmed with dilute nitric acid on the steam-bath it is oxidised as well as nitrated, and yields 5(or 8)-nitro-6 : 7-dimethoxy-2-methyl-1 : 2-dihydro*iso*quinolone (II and II*a*):


(I.)

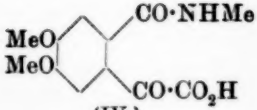

(II.)


(II*a*.)

Other substances, isolated from among the products of the oxidation of cryptopine with dilute nitric acid (D 1·22), are *m*-hemipinimide (III) and 3 : 4-dimethoxy-6-methylcarbamylphenylglyoxylic acid (IV) :


(III.)

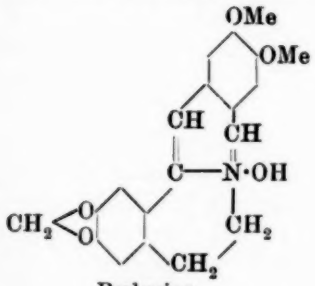
and

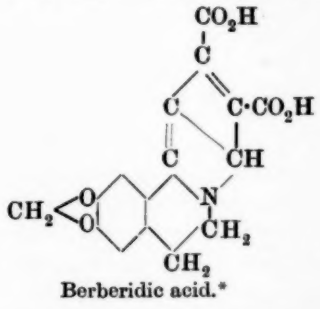

(IV.)

The last-mentioned substance had already been obtained by Mason and Perkin (T., 1914, **105**, 2018) from papaveraldine methosulphate by oxidation with permanganate, and its formation from cryptopine is important as affording valuable confirmation of the order in which the carbon and nitrogen atoms are attached to the dimethoxybenzene nucleus.

Dobbie and Marsden (T., 1897, **71**, 657) and Dobbie and Lauder (T., 1902, **81**, 145) have shown that the alkaloids berberine and corydaline yield, on oxidation with very dilute nitric acid (1 in 20) at the temperature of the steam-bath, acids derived from the alkaloids by the oxidation of one of the benzene nuclei and consequent formation of two carboxyl groups. Thus berberine, under these conditions, yields berberidic acid, $C_{16}H_{11}O_6N$, the dimethoxybenzene nucleus being destroyed in this case, and corydaline behaves in a similar manner.

Berberidic acid, although dibasic, behaves on titration as a monobasic acid and readily yields the silver hydrogen salt, $C_{16}H_{10}O_6NAg$,

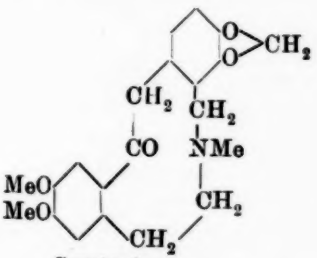

Berberine.


Berberidic acid.*

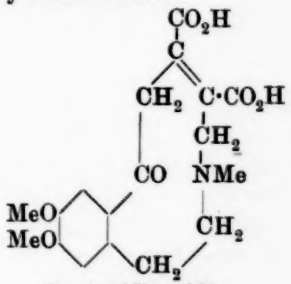
* The present author would venture to suggest that the constitution of berberidic acid is probably more accurately represented by the formula given below which obviates the para-linking and explains in a very simple

but the normal silver salt is obtained when its solution in ammonia is precipitated by silver nitrate. Since the formation and properties of this acid furnished so welcome a confirmation of the formula for berberine, which had been arrived at from other considerations, every effort was made to obtain the corresponding acid from cryptopine, and ultimately small quantities of a somewhat similar acid were with difficulty obtained under the rather unusual conditions described on p. 894. In these circumstances cryptopine yields a sparingly soluble precipitate which is mainly a mixture of nitrocryptopine, $C_{21}H_{22}(NO_2)O_5N$, and the new acid.

This acid, which has been named *cryptopidic acid*, has the composition $C_{18}H_{21}O_7N$, crystallises in yellow prisms melting at 185—187°, and resembles berberidic acid in many of its properties. Like berberidic acid, it behaves on titration as a monobasic acid, but that it is really dibasic is shown by the fact that it yields the normal silver salt, $C_{18}H_{19}O_7NAg_2$, when the slightly alkaline solution of the ammonium salt is precipitated by silver nitrate. Cryptopidic acid also exhibits feebly basic properties, since it yields the lemon-yellow hydrochloride, $C_{18}H_{21}O_7N,HCl$, and the almost colourless acetate, $C_{18}H_{21}O_7N,C_2H_4O_2$, when its solutions in the concentrated acids are allowed to crystallise, but these salts are readily dissociated by water. It still contains the two methoxy-groups of the original cryptopine molecule, a fact which makes it obvious that during its formation it is the methylenedioxybenzene nucleus which has been destroyed and given rise to the two carboxyl groups. The explanation of the conversion of cryptopine into cryptopidic acid is therefore probably that represented by the scheme:

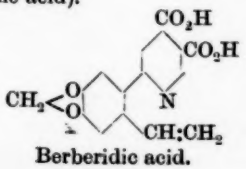


Cryptopine.

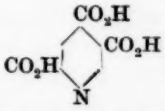


Cryptopidic acid.

manner, the oxidation of berberidic acid to berberonic acid (pyridine-2 : 4 : 5-tricarboxylic acid).

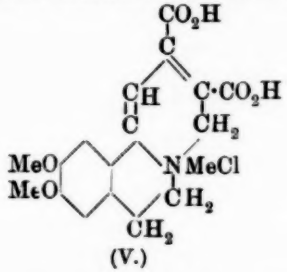


Berberidic acid.



Berberonic acid.

This formula is supported by the fact that it has not been found possible to obtain a pyridinetricarboxylic acid from cryptopidic acid by oxidation with permanganate, and this is in harmony with the absence of the pyrdine ring in the above formula. If, on the other hand, it should be found possible to convert cryptopidic acid into the chloride of *iso*cryptopidic acid (V) (compare the conversion of cryptopine into *iso*cryptopine chloride, p. 833), then this chloride might yield a pyridine derivative on oxidation.



(V.)

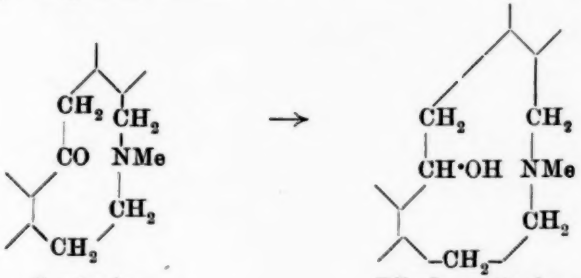
Unfortunately, cryptopidic acid is so difficult to prepare that experiments in this direction have so far been impossible. The action of concentrated nitric acid on cryptopine has also been investigated, and it is shown on p. 890 that this action results in the formation of two isomeric *dinitrocryptopines*, (*A*) *and* (*B*), $C_{21}H_{21}(NO_2)_2O_5N$, melting respectively at 250° and 213°. These very sparingly soluble substances crystallise well, and are characterised by the fact that their crystalline nitrates are almost insoluble in dilute nitric acid, whereas their sulphates and hydrochlorides are more readily soluble.

Dihydrocryptopine.

During the course of their experiments on cryptopine, Pictet and Kramers (*Ber.*, 1910, **43**, 1333) attempted to reduce the alkaloid by means of tin and hydrochloric acid, and since they recovered the unchanged substance after heating on the steam-bath for an hour, they concluded that cryptopine was incapable of reduction, and belonged therefore to the type of laudanosine rather than to that of papaverine.

At a later date Danckwortt (*Habilitationsschrift*, Breslau, 1912, p. 55; *Chem. Zentr.*, 1913, I, **84**, 432) showed, however, that cryptopine is reduced when its solution in excess of dilute sulphuric acid is boiled with sodium amalgam, and he isolated a substance melting at 182—183°, which was not analysed, but doubtless consisted of dihydrocryptopine, although not in a pure condition. During the present investigation considerable quantities of cryptopine have been reduced by a modification of the method employed by Danck-

wortt, and it is a curious fact that even when a very large excess of the reducing agent is employed the product always contains unchanged cryptopine, and the separation of this from the dihydrocryptopine was carried out by the fractional crystallisation of the oxalates as described on p. 932. The formation of dihydrocryptopine by the reduction of cryptopine is doubtless correctly represented by the partial scheme:

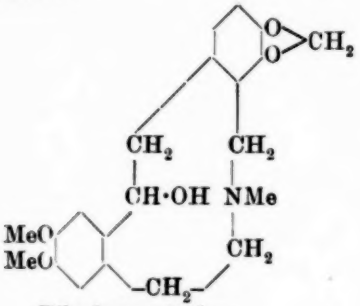


Cryptopine. Dihydrocryptopine.

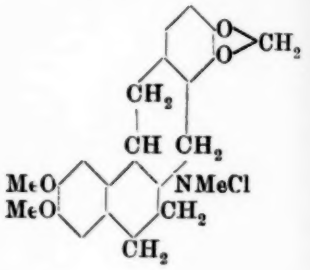
Dihydrocryptopine, $C_{21}H_{25}O_5N$, melts at 187—188°, and is a strong base, the salts of which, with mineral acids, are more readily soluble than those of cryptopine. When it is digested with acetyl chloride or phosphoryl chloride it undergoes an interesting change and yields two isomeric quaternary chlorides, $C_{21}H_{24}O_4NCl$, which have been named the α- and β-chlorides of *iso*dihydrocryptopine, and of these the α-chloride crystallises in prisms and is very readily soluble in water, whereas the β-chloride is sparingly soluble and crystallises as a voluminous mass of slender needles (compare pp. 933, 936). Cases similar to this have been previously observed by Voss and Gadamer (*Arch Pharm.*, 1910, **248**, 43; compare E. Schmidt, *ibid.*, 1894, **232**, 136), who obtained two quaternary methochlorides of *l*-canadine (*l*-tetrahydroberberine), which differed in solubility and melting point, and McDavid, Perkin, and Robinson (T., 1912, **101**, 1218) found that, when benzyl chloride is added to tetrahydroberberine, two tetrahydroberberine benzyl chlorides are produced, which also differ widely in properties.

Recently Pyman (T., 1913, **103**, 825) has shown that tetrahydroberberine, like *l*-canadine, also yields two methochlorides, and for the more soluble of these he suggested the prefix α-. These interesting cases of stereoisomerism are all due to the fact that the alkaloids which are capable of giving rise to the α- and β-quaternary chlorides contain both an asymmetric carbon and nitrogen atom, and Scholtz (*Ber.*, 1905, **38**, 595) has shown that coniine is, for the same reason, capable of yielding similar isomerides if its alkyl derivatives are combined with an iodide containing a different alkyl group, as, for example, in the case of *N*-ethylconiine allyl iodide, but that such is

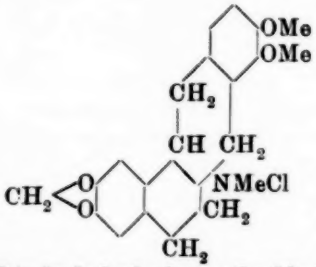
not the case when the two alkyl groups are the same, since then the asymmetry of the nitrogen atom does not occur. The mode of formation of the α- and β-quaternary chlorides of *iso*dihydrocryptopine will be evident from the scheme represented below, which also brings out clearly the striking resemblance between the formula of *iso*dihydrocryptopine chloride and that of tetrahydroberberine methochloride:



Dihydrocryptopine.



*iso*Dihydrocryptopine chloride.

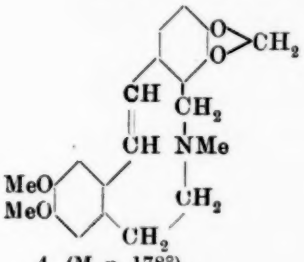


Tetrahydroberberine methochloride.

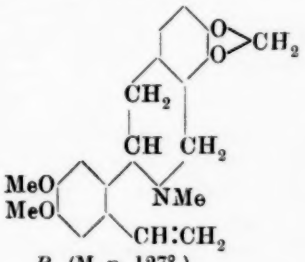
These quaternary chlorides of *iso*dihydrocryptopine and methyltetrahydroberberine differ only in the relative positions of the two methoxy- and the methylenedioxy-groups, and the closeness of this relationship becomes all the more remarkable when it is observed that the interchangeable groups occupy exactly the same positions in the upper and lower portions of the two formulæ. Yet it is clear that, although so very similar in structure, the two quaternary chlorides are not identical. In order to prove that the above view of the constitution of *iso*dihydrocryptopine chloride (α- and β-) is correct, a detailed careful comparison has been made between this chloride and tetrahydroberberine methochloride (α- and β-), with the result that the closest agreement in properties has been observed. When either of the *iso*dihydrocryptopine chlorides is digested with methyl-alcoholic potassium hydroxide, hydrogen chloride is eliminated and two *anhydrodihydrocryptopines*, *A* (m. p. 178°) and *B* (m. p. 127°), are produced, the former in the larger

quantity. These substances correspond exactly with the anhydrobases, *A* and *B*, which Pyman (T., 1913, **103**, 828) obtained by the dehydration of tetrahydroberberine methohydroxide, as the following comparison shows:

The Anhydrodihydrocryptopines.

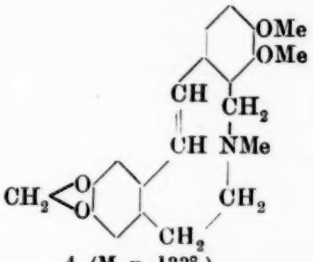


A. (M. p. 178°).

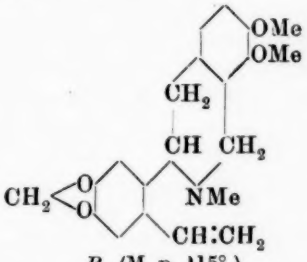


B. (M. p. 127°.)

The N-*Methyl*isotetrahydroberberines.

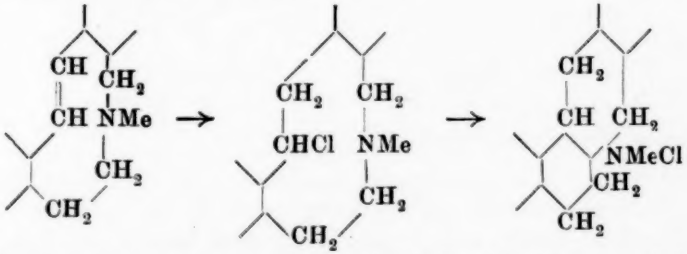


A. (M. p 133°.)



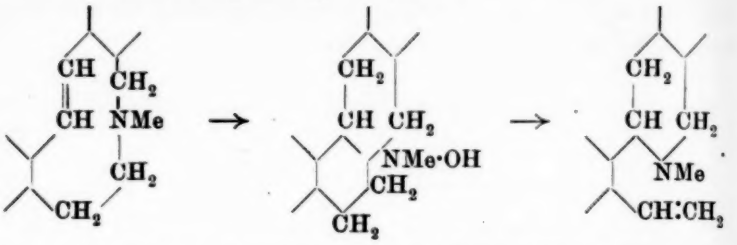
B. (M. p. 115°.)

In both cases the hydrochloride of *B* is much less readily soluble in dilute hydrochloric acid than that of *A*, and the bases *A* are converted into the quaternary chlorides of *iso*dihydrocryptopine and methyltetrahydroberberine respectively when they are digested with dilute hydrochloric acid, a change which probably takes place in accordance with the partial equation:



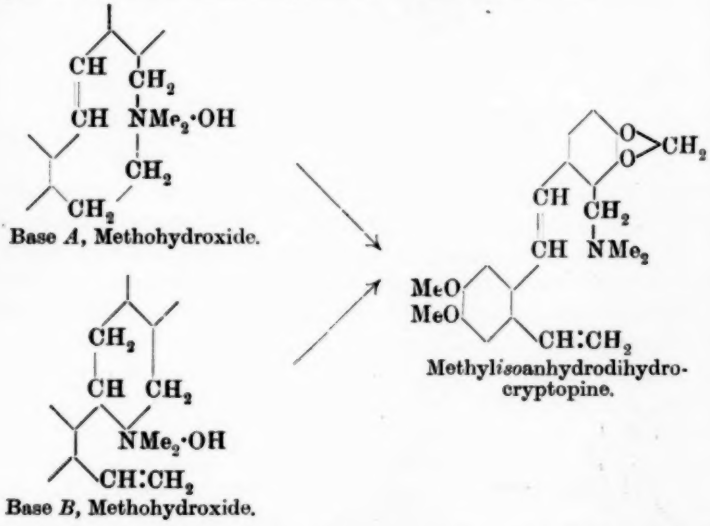
Again, the two bases, *A*, when digested with dilute alcohol, are

gradually converted, by the addition and subsequent elimination of water, into the corresponding bases, *B*:



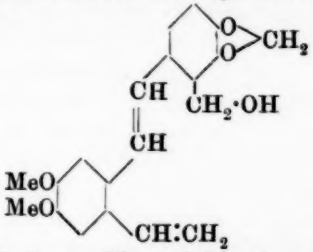
The further detailed comparison of the behaviour of the anhydrodihydrocryptopines (*A* and *B*) with that of the *N*-methyl*iso*tetrahydroberberines (*A* and *B*), which is described in the experimental part of the present investigation (pp. 945, 950), emphasises the remarkable resemblance exhibited by these two series of substances.

Anhydrodihydrocryptopine (*A*) readily combines with methyl sulphate, yielding a crystalline methosulphate, $C_{21}H_{23}O_4N,Me_2SO_4$, which, when digested with methyl-alcoholic potassium hydroxide, is readily decomposed with the formation of methyl*iso*anhydrodihydrocryptopine, and the same substance is also obtained when the methosulphate of base *B* is decomposed in a similar manner:



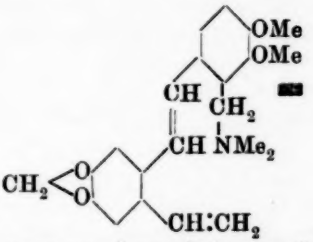
*Methyl*isoanhydrodihydrocryptopine melts at 106°, and the crystals are characterised by possessing a beautiful lilac fluorescence reminiscent of that of anthracene; it combines readily with methyl sulphate, and the crystalline methosulphate is decomposed by boil-

ing with methyl-alcoholic potassium hydroxide with elimination of trimethylamine and formation of α- and β-*iso*cryptopidol, $C_{20}H_{20}O_5$:

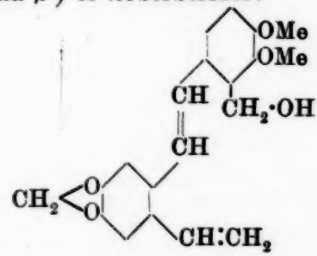


α-iso*Cryptopidol* is readily soluble in alcohol and melts at 90—92°, whereas the β-modification is sparingly soluble and does not melt at 250°.

An exactly similar behaviour is exhibited by the *A* and *B* modifications of methyl*iso*tetrahydroberberine, which also yield crystalline methosulphates readily decomposed by methyl-alcoholic potassium hydroxide with the formation of *dimethyl*iso*tetrahydroberberine*:



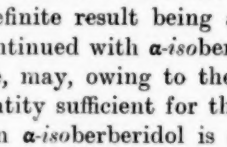
The almost exact correspondence between the properties of *N*-dimethyl*iso*tetrahydroberberine and those of methyl*iso*anhydrodihydrocryptopine is very striking; thus the crystals of both exhibit the same lilac fluorescence, and to the same extent, and the salts of the two bases can scarcely be distinguished from one another. Lastly, the methosulphate of *N*-dimethyl*iso*tetrahydroberberine behaves exactly like that of methyl*iso*anhydrodihydrocryptopine, since it is readily decomposed by methyl-alcoholic potassium hydroxide with elimination of trimethylamine and formation of two modifications (α- and β-) of *iso*berberidol:



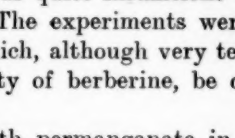
α-iso*Berberidol* is readily soluble in alcohol and melts at 88—90°, whereas the sparingly soluble β-modification decomposes at 250° and is doubtless identical with the substance, called berberilene,* which McDavid, Perkin, and Robinson (T., 1912, **101**, 1226) obtained by the action of aqueous potassium hydroxide on anhydro-*N*-benzyl*iso*tetrahydroberberine methochloride.

Since α-*iso*cryptopidol may be considered as the parent substance of cryptopine it was thought interesting and desirable that its constitution should be checked by determining the nature of the substances produced when it is submitted to the action of oxidising agents. Unfortunately, although experiments with this object in view were attempted, it was found that the decomposition was so complex that the available material was quite insufficient to allow of a definite result being achieved. The experiments were therefore continued with α-*iso*berberidol, which, although very tedious to prepare, may, owing to the accessibility of berberine, be obtained in quantity sufficient for the purpose.

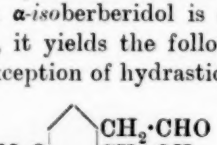
When α-*iso*berberidol is oxidised with permanganate in acetone solution, it yields the following substances, all of which, with the single exception of hydrastic acid, had not previously been obtained:



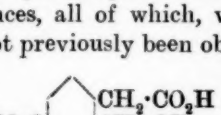
ω-Hydroxy 3 : 4-dimethoxy-*o*-tolylacetaldehyde. (M. p. 58°.)



ω-Hydroxy-3 : 4-dimethoxy-*o*-tolylacetic acid. (M. p. 125°).



4-Keto-5 : 6-dimethoxy-dihydro*iso*coumarin. (M. p. 190°.)



Hydrastic acid. (M. p. 180°.)

It will be seen that the formation of these substances is in agreement with, and may be considered as confirmation of, the constitutional formula for *iso*berberidol, and indirectly of that of *iso*cryptopidol, which have been represented above.

The Methylcryptopines.

The investigation of these derivatives was due, in the first place, to the observation that cryptopine methochloride, $C_{21}H_{23}O_5N,MeCl$, is decomposed by boiling sodium hydroxide with elimination of

* The name berberidol appears to the author to be preferable, because it indicates the alcoholic nature of the substance.

hydrogen chloride and formation of a methylcryptopine, $C_{22}H_{25}O_5N$, which melts at 110°.

Subsequently it was found that cryptopine methosulphate, $C_{21}H_{23}O_5N,Me_2SO_4$, is rapidly hydrolysed when it is digested with methyl-alcoholic potassium hydroxide, and in this case the main product is a methylcryptopine melting at 153°, but varying, although usually very small quantities of the modification melting at 110° and of a third modification melting at 128° are always produced at the same time. For the sake of convenience, these three modifications have been named α-, β-, and γ-; methylcryptopine (α) melts at 153°, methylcryptopine (β) at 128°, and methylcryptopine (γ) at 110°. Of these three varieties the α-modification is completely converted, by boiling with methyl alcohol, into the β-modification, whereas the reverse change is brought about by dissolving the β-modification in dilute hydrochloric acid and then precipitating with ammonia. Dr. N. V. Sidgwick was kind enough to examine these two modifications by the method which he has described (T., 1915, **107**, 678) for distinguishing tautomeric, isomeric, and polymeric from polymorphic substances, and obtained results which prove that the methylcryptopines, α- and β-, are polymorphic forms of the same substance, while γ- is isomeric with them.

The detailed examination of the methylcryptopines β- and γ-, melting at 128° and 110° respectively, has shown that they differ widely, not only in their physical characteristics, the β-modification being, for example, much less readily soluble than the γ-, but also in many of their chemical properties. Methylcryptopine (β) does not yield an oxime or semicarbazone, and, when digested with acetic anhydride, it does not appear to yield an acetyl derivative. It yields, however, a characteristic, crystalline *methosulphate*, $C_{22}H_{25}O_5N,Me_2SO_4$, and this decomposes, on boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of *cryptopidiol*, an amorphous substance which does not melt at 250°, and *anhydrocryptopidiol*, which is crystalline and melts at 105°:

$$C_{22}H_{25}O_5N,Me_2SO_4 \longrightarrow C_{22}H_{25}O_5N,MeOH \longrightarrow$$

$$\underset{\text{Cryptopidiol.}}{C_{20}H_{20}O_6} \quad \text{and} \quad \underset{\text{Anhydrocryptopidiol.}}{C_{20}H_{18}O_5} \quad \text{and} \quad NMe_3.$$

Unlike the β-modification, methylcryptopine (γ) yields an *oxime*, $C_{21}H_{25}O_4N(C{:}N{\cdot}OH)$, which has, so far, only been obtained in the form of a syrup; the *semicarbazone*, however,

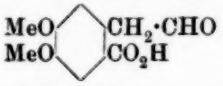
$$C_{21}H_{25}O_4N(C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2),$$

is a crystalline substance and melts at 185°. Unlike the β-modification, methylcryptopine (γ) reacts readily with acetic anhydride with the formation of the *acetyl* derivative, $C_{22}H_{24}O_4(O{\cdot}CO{\cdot}CH_3)N$,

which is crystalline, melts at 95°, and is characterised by the beauty of its salts, which separate from water in brilliant, glistening scales. This acetyl derivative is readily hydrolysed by methyl-alcoholic potassium hydroxide, and methylcryptopine (γ) is regenerated. The *methosulphate*, $C_{22}H_{25}O_5N,Me_2SO_4$, unlike the corresponding derivative of methylcryptopine (β), exhibits little facility for crystallisation, but, when it is digested with methyl-alcoholic potassium hydroxide, it decomposes in exactly the same manner as the latter with elimination of trimethylamine and formation of a mixture of cryptopidiol and anhydrocryptopidiol. When methylcryptopine (γ) is oxidised by permanganate, the main product is a very sparingly soluble, amorphous acid the composition of which, in spite of careful investigation, is still doubtful. The mother liquors from this contain small quantities of a neutral substance, which crytsallises well from water, melts at 175°, and has the formula $C_{11}H_{12}O_5$. This substance contains two methoxy-groups, yields a well-characterised acetyl derivative,

$$C_{11}H_{11}O_4\cdot O\cdot CO\cdot CH_3$$

(m. p. 150°), and is a hydroxylactone. It dissolves in boiling dilute alkali hydroxides with the formation of salts of the corresponding acid, which, however, is not stable, since the addition of acids to the solution of its salts produces a clear liquid, from which the lactone gradually separates at the ordinary temperature. It is obvious that there are two possible formulæ for the acid, namely:



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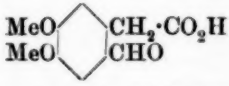
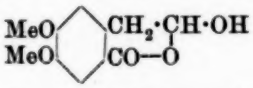


,

and, although there is no sufficient reason to decide between these, the first formula is preferred for various reasons connected more particularly with the behaviour of berberidol on oxidation (compare p. 844), and the substance, $C_{11}H_{12}O_5$, will therefore be considered as the lactone of 4:5-dimethoxyphenylacetaldehyde-2-carboxylic acid. This hydroxy-lactone and its acetyl derivative may then be represented thus:



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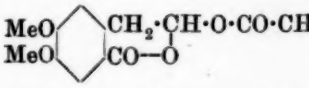

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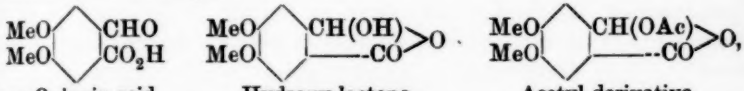
Since this hydroxy-lactone is obviously a substance of considerable interest, it is unfortunate that, owing to the very small quantity of available material, it could not be more fully investigated. Experiments on the synthesis of substances of this type are, however, in progress, but the problem is a very difficult one. The readiness with which the aldehydo-acid yields the hydroxy-lactone is interesting when considered in connexion with the conditions of

lactone formation in the series of the opianic acids. It is well known that the opianic acids, while existing in the free state, readily yield acetyl derivatives of the corresponding hydroxy-lactones, for example:



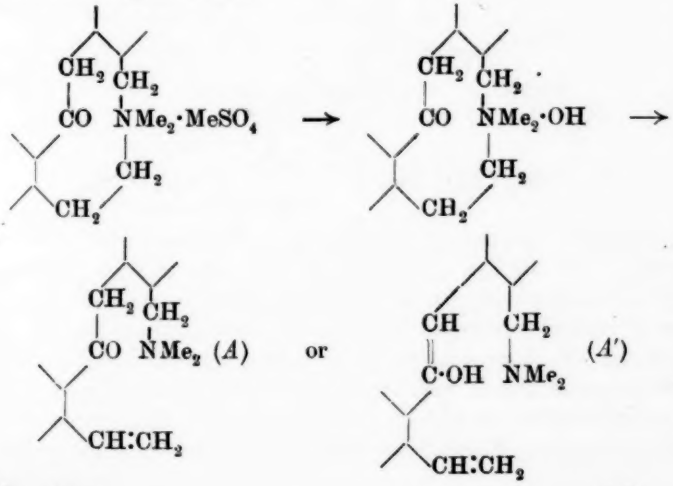
m-Opianic acid. Hydroxy-lactone. (unknown). Acetyl derivative.

and, in the case of ordinary opianic acid, isomeric esters have been obtained, derived from the acid and the hydroxy-lactone respectively (compare Wegscheider, *Monatsh.*, 1896, **17**, 111). The actual hydroxy-lactones of the opianic acids have, however, so far not been isolated, and do not appear to be capable of existence. In the latter respect the opianic acids differ from their reduction products, the meconinic acids, $(MeO)_2C_6H_2(CH_2{\cdot}OH){\cdot}CO_2H$, which are characterised by the ease with which they are converted into the corresponding meconines.

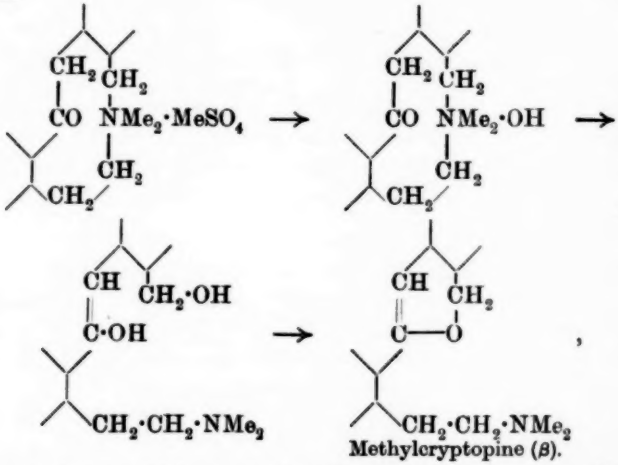
The fact that 4:5-dimethoxyphenylacetaldehyde-2-carboxylic acid, $C_{11}H_{12}O_5$, is incapable of existence, and at once passes into the iscmeric hydroxy-lactone, is the more remarkable in view of the fact that the latter substance is a δ-lactone.

Constitution of the Methylcryptopines.

If the formula for cryptopine advanced on p. 831 is accepted as correct, the most direct way to deduce the constitution of a methylcryptopine is to assume that the decomposition of the methosulphate of cryptopine by means of potassium hydroxide proceeds normally in the following manner:



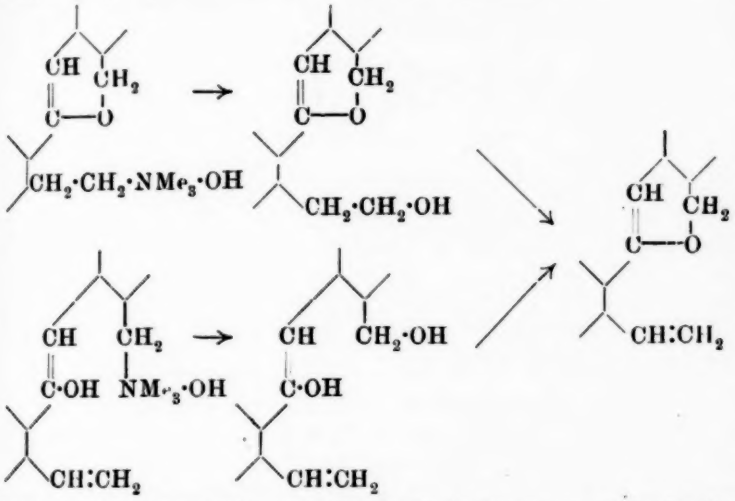
Careful consideration of the expression *A* leads to the conclusion that it is in complete harmony with all the known properties of methylcryptopine (γ) (m. p. 110°); thus it accounts for the fact that this substance yields an oxime and a semicarbazone, and the formation of the acetyl derivative is readily understood if it is assumed that the substance is capable of reacting in its enolic modification, *A'*. Furthermore, this formula is in agreement with the conversion of methylcryptopine (γ) into the *epi*methylcryptopines and the relationship of these to the *epi*cryptopines (p. 870). The development of a satisfactory constitutional formula for methylcryptopine (β) (m. p. 128°) is not so simple. Careful examination of the properties of this substance makes it obvious that it cannot be a mere stereoisomeric modification of the enolic formula, *A'*, a supposition which is improbable in any case, since the transient change of this formula into the keto-modification, *A*, would at once destroy the stereoisomerism, and, so far, it has not been found possible to convert methylcryptopine (β) into the (γ)-modification, or vice versa. Consideration of all the properties of methylcryptopine (β) leaves scarcely any doubt that its formation from cryptopine methosulphate by the action of alkali takes place according to the scheme:



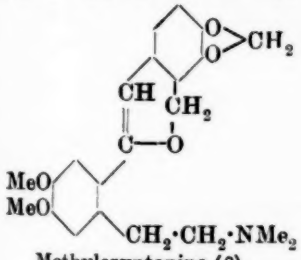
Methylcryptopine (β).

This suggested partial expression for methylcryptopine (β) is in harmony with all the properties of this substance, and affords a ready explanation of the striking differences in its properties and those of methylcryptopine (γ). Thus, whereas the latter (γ) does, the former (β) does not, yield an oxime, semicarbazone, or acetyl derivative, and this is well accounted for in the suggested formula for methylcryptopine (β) by the absence both of a carbonyl and a hydroxy-group. Support for these views as to the constitutions of

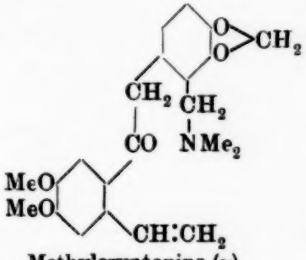
the methylcryptopines may be discovered in the fact that methylcryptopine (β) and (γ) yield the same substances—cryptopidiol and anhydrocryptopidiol—on exhaustive methylation:



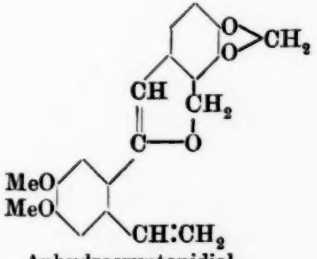
The formula for anhydrocryptopidiol is in harmony with the fact that this substance does not yield an acetyl derivative when it is digested with acetic anhydride. If the above partial formulæ are developed, the expressions for the methylcryptopines and for anhydrocryptopidiol will appear as follows:



Methylcryptopine (β).

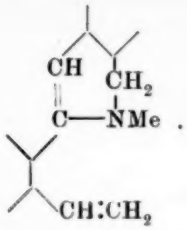


Methylcryptopine (γ).



Anhydrocryptopidiol.

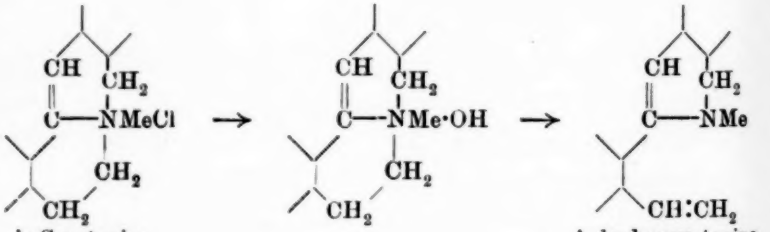
Anhydrocryptopine,



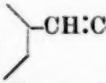
In the whole range of the derivatives of cryptopine the substance which has proved to be of the greatest interest, on account of the remarkable decompositions which it undergoes, is anhydrocryptopine. This substance is obtained when *iso*cryptopine chloride (p. 833) or the corresponding sulphate is digested with methyl-alcoholic potassium hydroxide, hydrogen chloride being eliminated according to the equation:

$$\underset{\substack{\textit{iso}\text{Cryptopine}\\ \text{chloride.}}}{C_{21}H_{22}O_4NCl} = \underset{\text{Anhydrocryptopine.}}{C_{21}H_{21}O_4N} + HCl.$$

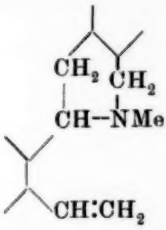
Anhydrocryptopine is a beautifully crystalline, pale yellow substance, melts at 110—111°, and yields lemon-yellow salts with mineral acids, which, with the exception of the hydriodide, $C_{21}H_{21}O_4N,HI$, and the platinichloride, $(C_{21}H_{21}O_4N)_2H_2PtCl_6$, are readily soluble. The explanation of the formation of anhydrocryptopine follows the usual lines, and leads directly to a constitutional formula for that substance which is in harmony with all its properties:



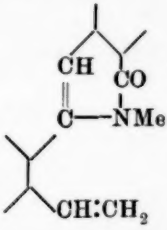
*iso*Cryptopine chloride. Anhydrocryptopine.

The presence of the grouping,  , in the nitrogen ring affords an explanation for the readiness with which anhydrocryptopine couples with diazonium salts, and the facts that reduction with sodium amalgam in acid solution converts anhydrocryptopine into anhydrodihydrocryptopine (*B*), $C_{21}H_{23}O_4N$ (m. p. 127°, compare

p. 841), and the oxidation by permanganate produces ketoanhydrocryptopine, $C_{21}H_{19}O_5N$ * (*m.* p. 163°, p. 986):



and



are easily understood with the aid of the expression suggested for anhydrocryptopine. Anhydrodihydrocryptopine (*B*) has also been obtained from *iso*dihydrocryptopine chloride by the action of methyl-alcoholic potassium hydroxide,

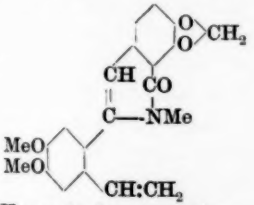
$$C_{21}H_{23}O_4NCl = H_{21}H_{23}O_4N + HCl,$$

and its properties are described in detail on pp. 941–944.

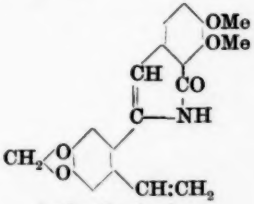
Ketoanhydrocryptopine does not yield salts with dilute mineral acids; its solution in acetic acid is dissociated on the addition of water, and these very feeble basic properties are in harmony with the proximity of the CO group to the nitrogen atom. On oxidation with permanganate, ketoanhydrocryptopine yields a curious acid, $C_{20}H_{17}O_7N$, which has been named norketoanhydrocryptopic acid, and this acid is converted by boiling with anhydrous formic acid into an almost insoluble, crystalline mass, $C_{20}H_{15}O_6N$, water being eliminated during the process.

This dehydronorketoanhydrocryptopic acid is not an ordinary anhydride, since it is not possible to regenerate the acid by boiling it with alkali hydroxides in aqueous or alcoholic solution. It is therefore suggested that its formation is due to internal condensation between the carboxyl and the reactive hydrogen atom of the -CH:C- group in the molecule of the acid:

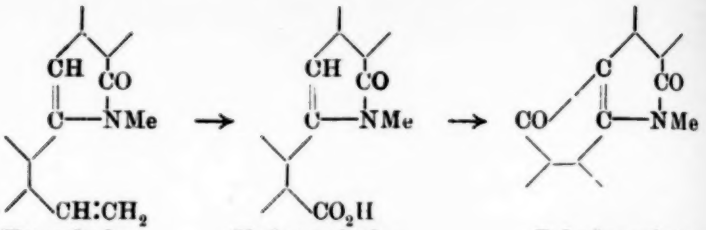
* Ketoanhydrocryptopine corresponds very closely with *iso*oxyberberine, which Bland, Perkin, and Robinson (T. 1912, **101**, 262) obtained from oxyberberine by the action of dilute hydrochloric acid:



Ketoanhydrocryptopine.



*iso*Oxyberberine.



Ketoanhydrocryptopine. Norketoanhydrocryptopic acid. Dehydronorketoanhydrocryptopic acid.

Ketoanhydrocryptopine is also characterised by its conversion into the splendid scarlet keto*isoepi*cryptopirubin hydrochloride by the action of phosphoryl chloride, a change which is discussed in detail on p. 874.

It has already been stated that anhydrocryptopine undergoes an extraordinary variety of changes when it is treated with ordinary reagents, and the conversion of this substance into (i, p. 860) the hydrochlorides of the hydroxy*iso*anhydrodihydrocryptopines and into *iso*anhydrocryptopine by the action of dilute hydrochloric or sulphuric acids (ii, p. 865), the *epi*cryptopines by the action of concentrated hydrochloric acid, and into the scarlet *epi*cryptopirubin salts by the subsequent action of phosphoryl chloride, and (iii, p. 855) into the methoxy- and ethoxy-derivatives of anhydrocryptopine by simply boiling with methyl or ethyl alcohols respectively, have been made the subjects of special chapters. Still more remarkable and difficult to understand than the changes just mentioned are the interactions which occur when anhydrocryptopine is treated, under ordinary conditions, with such reagents as methyl sulphate or methyl iodide. Thus, for example, anhydrocryptopine combines, apparently in the normal manner, with methyl sulphate when the substances are simply warmed together, and the resulting *anhydrocryptopine methosulphate*, $C_{21}H_{21}O_4N,Me_2SO_4$, is a colourless, crystalline substance which, in outward appearance, is exactly similar to the many other methosulphates described in this communication. When, however, this substance is digested with methyl-alcoholic potassium hydroxide, it does not behave in the normal manner and yield methylanhydrocryptopine, but decomposes with the elimination of both methyl groups and regeneration of anhydrocryptopine. In order to obtain some clue to this extraordinary change, which, so far as the author is aware, had not previously been observed in the case of any other methosulphate, the corresponding methiodide, $C_{21}H_{21}O_4N,MeI$, was prepared (i) from the methosulphate by the action of potassium iodide, and (ii) by the direct union of anhydrocryptopine with methyl iodide, and, so far as could be determined, the same substance, melting at 188—190°,

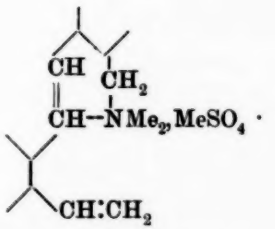
is produced in each case. When this sparingly soluble methiodide was converted by the action of silver chloride into the readily soluble methochloride, and this digested with methyl-alcoholic potassium hydroxide, decomposition again took place with elimination of the methyl group, and anhydrocryptopine was regenerated.

Still more remarkable, perhaps, is the fact that concentrated hydrochloric acid is also able to bring about the removal of the methyl group. Thus, for example, when anhydrocryptopine methosulphate is boiled for a few minutes with concentrated hydrochloric acid it is converted almost quantitatively, and with elimination of both the methyl groups of the methyl sulphate, into a new quaternary chloride, $C_{21}H_{22}O_4NCl$, called *ψ-cryptopine chloride* (p. 984), and the same change takes place when anhydrocryptopine methochloride is digested with concentrated hydrochloric acid:

I. $C_{21}H_{21}O_4NMe,MeSO_4 + 2H_2O + HCl = C_{21}H_{22}O_4NCl + 2MeOH + H_2SO_4.$

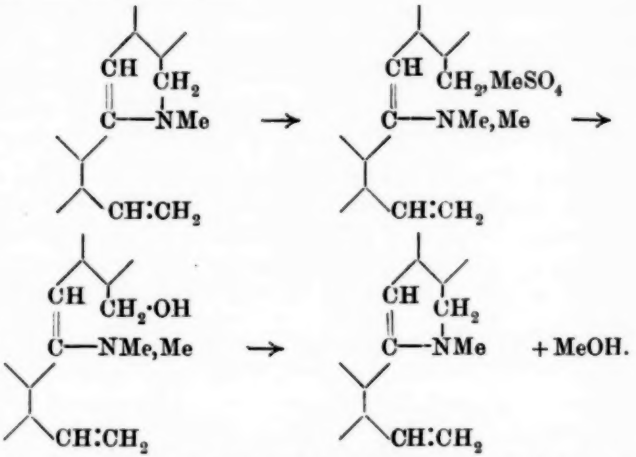
II. $C_{21}H_{21}O_4N,MeCl + H_2O = C_{21}H_{22}O_4NCl + MeOH.$

If an attempt is made to explain these remarkable changes it will at once be granted that as anhydrocryptopine methosulphate exhibits towards alkalis and acids a behaviour so much at variance with that which has been always observed in analogous cases, the tendency is to conclude that it cannot have the normal structure (I):



It should, however, be remembered that examples of the removal of alkyl groups from nitrogen by similar means are not uncommon, and, among these, perhaps the best case to cite, because of its close connexion with anhydrocryptopine, is that of dimethylaniline. When this substance is heated in a stream of hydrogen chloride at about 280° it loses first one and then the second methyl group with the formation of methylaniline and aniline respectively. Still more remarkable and more directly analogous to the action of alkalis on anhydrocryptopine methosulphate is the fact that phenyltrimethylammonium iodide, $C_6H_5 \cdot NMe_3I$, is decomposed, simply by boiling with aqueous potassium hydroxide, with elimination of methyl alcohol and formation of dimethylaniline. Such analogies

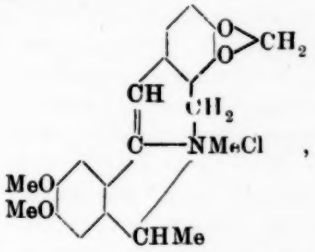
clearly indicate that it is possible to explain the curious behaviour of anhydrocryptopine methosulphate towards acids and alkalis by employing the normal formula, but the fact that the elimination of methyl, which takes place in these cases, is so entirely unknown in the case of normal methosulphates suggests that anhydrocryptopine methosulphate may have an unusual structure. It is possible, for example, that, owing to the weak basic nature of anhydrocryptopine, the nitrogen atom cannot attach the elements of methyl sulphate or methyl iodide directly, and, in order that addition may take place, fission between the $-CH_2-$ and the $>NMe$ groups is necessary. On subsequent hydrolysis with concentrated methyl-alcoholic potassium hydroxide, methyl alcohol might then be eliminated and the union remade:



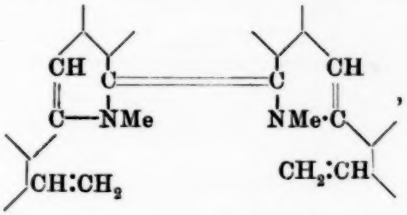
That anhydrocryptopine has comparatively little tendency to yield *N*-additive products is shown by the experience that, whilst it will react moderately readily with methyl iodide or methyl sulphate, it does not combine with ethyl bromide or ethyl sulphate, and only to a very slight extent with ethyl iodide. Every effort was made to obtain such ethyl derivatives because of the interest which attached to the determination whether anhydrocryptopine ethosulphate, for example, would, on hydrolysis with alcoholic potassium hydroxide, lose an alkyl group as the methosulphate does, and, if so, whether the process would result in the formation of anhydrocryptopine or the corresponding ethyl analogue.

It has already been mentioned that anhydrocryptopine methosulphate is decomposed by boiling with concentrated hydrochloric acid with elimination of a methyl group and formation of a quaternary chloride, $C_{21}H_{22}O_4NCl$, called ψ-cryptopine chloride, which is isomeric with *iso*cryptopine chloride (p. 833). This salt

crystallises in pale ochreous needles, has no definite melting point, and yields with potassium iodide the beautifully crystalline ψ-cryptopine iodide, $C_{21}H_{22}O_4NI$, which melts at 232—235°. ψ-Cryptopine chloride does not give a precipitate when dilute ammonia is added to its aqueous solution, but when boiled with sodium hydroxide, it yields a base which is green at first and in contact with air becomes intense blue, then green, and finally almost black. In this respect it differs in a marked manner from the other quaternary chlorides described in this communication, such, for example, as *iso*cryptopine chloride and *iso*dihydrocryptopine chloride (p. 840), which decompose normally with acids yielding colourless anhydro-bases. Taking into account the isomerism of ψ-cryptopine chloride and *iso*cryptopine chloride and the fact that it combines with diazonium salts, there can scarcely be a doubt that the constitution of ψ-cryptopine chloride is that represented by the formula:

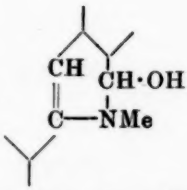


and the black base would then have the double molecule:



(compare p. 874).

Hydroxyanhydrocryptopine,



and its Derivatives.

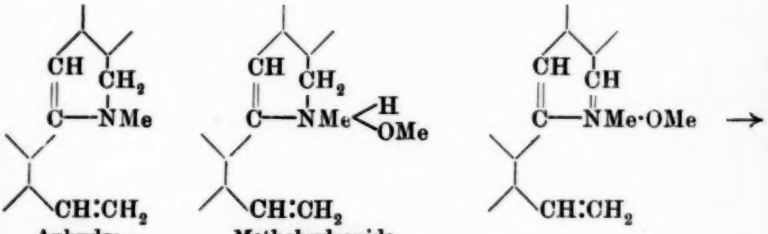
A very characteristic property of anhydrocryptopine is its behaviour towards alcohols. When, for example, the finely powdered substance is boiled with methyl alcohol for a couple of

minutes and the solution rapidly filtered, a yellow solution is obtained, from which anhydrocryptopine crystallises, on cooling, with little loss. If, however, the boiling is continued, the liquid gradually darkens, becomes deep brown, and then a portion only of the anhydrocryptopine separates on cooling.

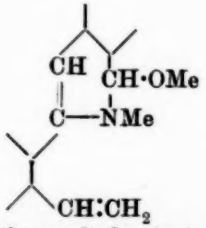
In order to obtain some explanation of this change, a careful investigation was made, when it was found that the deep brown solution always contains two isomeric substances, $C_{22}H_{23}O_5N$, which melt at 188° and 162° respectively, and these have been named the *methoxyanhydrocryptopines* (*A*) and (*B*). These substances are produced from anhydrocryptopine by the addition of methyl alcohol and loss of two atoms of hydrogen:

$$C_{21}H_{21}O_4N + CH_3{\cdot}OH - 2H = C_{22}H_{23}O_5N,$$

and the necessary oxidation is certainly brought about, in part at least, by the action of the air. The careful investigation, more particularly of the (*A*) modification, gave results which, for a long time, were difficult to understand, but there can scarcely be a doubt that the following explanation, which was kindly suggested by Professor Robinson, is to be accepted as the correct one. In the first place, the molecule of anhydrocryptopine adds on methyl alcohol at the nitrogen atom, yielding anhydrocryptopine methohydroxide, and this dihydro*iso*quinoline derivative then undergoes oxidation to the corresponding *iso*quinoline derivative with the loss of two atoms of hydrogen:



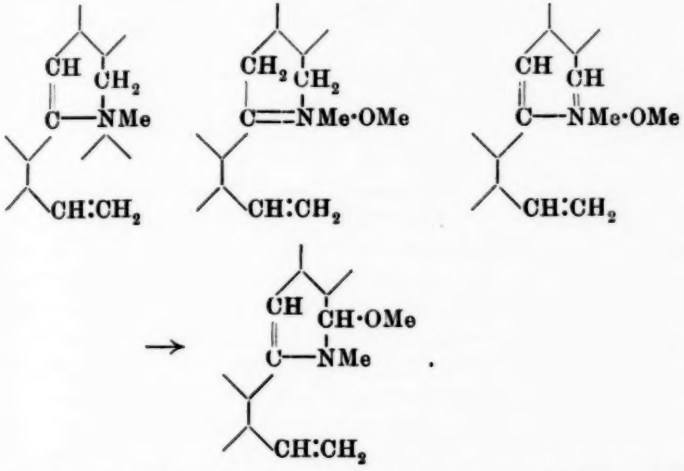
Anhydrocryptopine. Methohydroxide.



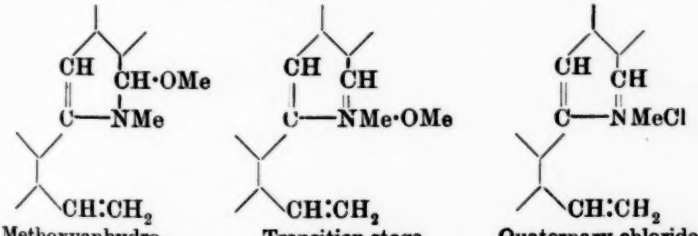
Methoxyanhydrocryptopine.

A rather different way of arriving at the same result is the following:

If the free valencies of the quinquevalent nitrogen atom are represented, it will be seen that, together with the ethylenic linking, they make up a conjugated system of double linkings, and the methyl alcohol may then add itself to this in the usual way, oxidation subsequently taking place:



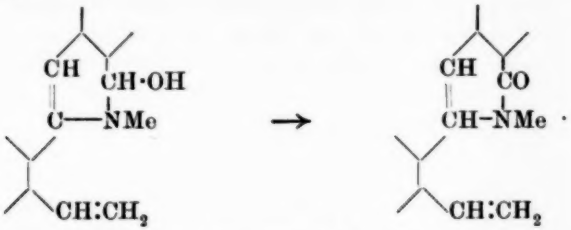
There is no difficulty in accepting the ready oxidation of the dihydro*iso*quinoline derivatives first formed in each case, as experience shows that such substances have a great tendency to become oxidised to the corresponding quinoline type. Methoxyanhydrocryptopine (*A*) dissolves in dilute hydrochloric acid with loss of methyl alcohol, whereby it is converted into the deep yellow, quaternary *chloride* of *hydroxyanhydrocryptopine*, $C_{21}H_{20}O_4NCl$, and from this the brilliant orange *iodide*, $C_{21}H_{20}O_4NI$, may be prepared by the addition of potassium iodide:



Methoxyanhydrocryptopine. Transition stage. Quaternary chloride

Hydroxyanhydrocryptopine, $C_{21}H_{21}O_5N$, is obtained by adding sodium hydroxide (but not dilute ammonia) to the solution of the chloride, as an almost colourless, chalky precipitate, which, so far, has not been obtained in the crystalline condition, and this base,

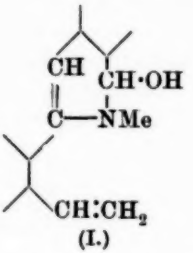
on oxidation with permanganate, yields ketoanhydrocryptopine (compare p. 851):



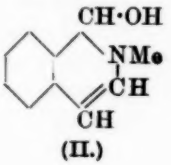
One of the most striking properties of hydroxyanhydrocryptopine is the fact that the amorphous base, when warmed with methyl alcohol, immediately crystallises, owing to its conversion into the sparingly soluble methoxyanhydrocryptopine (m. p. 188°). In this and in many other respects hydroxyanhydrocryptopine (I) shows the closest resemblance to *iso*quinoline methohydroxide (II), cotarnine (III), and also to berberine (IV), and this is perhaps not surprising if the formulæ for these substances are placed side by side, when it is at once seen that the same reactive grouping:

$$-CH(OH)\cdot NMe- \quad \text{or} \quad -CH(OH)\cdot N\cdot CH_2-,$$

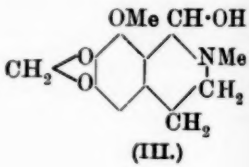
is contained in all of them:



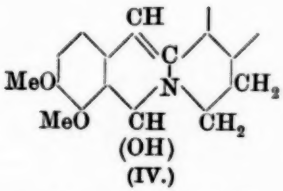
(I.)



(II.)



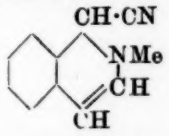
(III.)



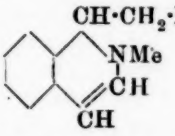
(IV.)

These substances all combine with alcohols to form the corresponding alkyl derivatives, and are also characterised by the ease with which they yield condensation products with a great variety of substances, such as hydrocyanic acid, alcohols, ketones, nitromethane, trinitrotoluene, etc. In such cases the condensation takes place between the $-CH(OH)-$ group and the reactive hydrogen atom of the second substance; *iso*quinoline methohydroxide, for

example, yields with hydrocyanic acid and nitromethane the following derivatives:



and



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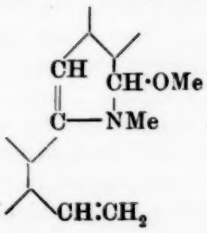
and derivatives of this type have also been obtained from hydroxyanhydrocryptopine.

When anhydrocryptopine is digested with methyl alcohol, two methoxyanhydrocryptopines, (*A*) and (*B*), are always produced, and of these the less readily soluble, (*A*), melts at 188°, whereas the more readily, but still sparingly soluble, isomeride, (*B*), melts at 152°.

These substances, on treatment with hydrochloric acid and subsequently with sodium hydroxide, yield apparently, as might indeed be expected, the same hydroxyanhydrocryptopine. It is, of course, possible that these isomerides are merely polymorphic modifications of the same substance, but they persistently crystallise unchanged from methyl alcohol, even when the supersaturated solution of the one is seeded with a crystal of the other modification. In only one case has the partial conversion of the modification (*B*) into (*A*) been accomplished, and that was when the former was boiled for half an hour with a quantity of methyl alcohol insufficient to dissolve it completely. The small amount of undissolved substance was found to melt at about 175°, and evidently consisted of the impure modification (*A*), whereas the mother liquor, on concentration, yielded a crop of the almost pure modification (*B*). The small amount of these cryptopine derivatives which were available made a more extended investigation impossible, but the author is inclined to the opinion that the substances (*A*) and (*B*) are really isomeric, and not merely polymorphic, modifications. Such isomerism is possible if the Hantzsch-Werner hypothesis—which in the case of the oximes concerns the position of the hydroxyl group in relation to the plane of the double linking—is extended, as indeed it must be, to the case of the nitrogen atom in the ring as in

. If this is done, it is clear that methoxyanhydrocryptopine,



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might well be expected to exist in stereoisomeric modifications, and it is conceivable that the forms (*A*) and (*B*) are actually such modifications (compare T. S. Moore, P., 1914, **30**, 182). In other cases of this kind the isomeric modifications may actually not have been observed owing to change of configuration into the more stable form under the influence of the reagents required for their preparation. In the case of methoxyanhydrocryptopines, however, the only reagent used in their preparation and separation is methyl alcohol, and so mild an agent might quite possibly exhibit no tendency to bring about molecular rearrangement.

*The Hydroxy*iso*anhydrodihydrocryptopines and* iso*Anhydrocryptopine.*

In the next chapter (p. 865), the conversion of anhydrocryptopine into the *epi*cryptopines by the action of *concentrated* hydrochloric acid is described, and it was the difficulty of interpreting the remarkable results obtained under these conditions which led to the long and difficult investigation of the behaviour of anhydrocryptopine with *dilute* hydrochloric acid and subsequently with dilute sulphuric acid.

Dilute acids, like concentrated acids, bring about the hydration of anhydrocryptopine, $C_{21}H_{21}O_4N$, and lead to the formation of substances, $C_{21}H_{23}O_5N$, which contain one molecule of water more and are isomeric with cryptopine and the *epi*cryptopines. It is very remarkable that the reaction with dilute acids proceeds in an entirely different direction from that observed in the case of concentrated acids, and this may in part be due to the observation that, whereas concentrated acids react very rapidly, the action of dilute acids is a much slower one and obviously of quite a different kind. In order to make this difficult matter clear, it will be well to summarise the chief characteristics of this change and the properties of the substances produced.

(1) Boiling with dilute hydrochloric acid converts anhydrocryptopine into the hydrochlorides of two isomeric hydroxy*iso*anhydrodihydrocryptopines, (*A*) and (*B*), which melt respectively at 227° and 117°.

(2) The hydrochloride (*A*) yields, with ammonia, hydroxy*iso*anhydrodihydrocryptopine (*A*), and this amorphous base is again converted into the crystalline hydrochloride (*A*) by solution in dilute hydrochloric acid.

(3) The hydrochloride (*B*) behaves in a similar manner, and yields with ammonia hydroxy*iso*anhydrodihydrocryptopine (*B*), which is also amorphous and is again converted into the hydrochloride (*B*) by solution in dilute hydrochloric acid.

(4) The hydrochloride (*A*) is converted into the isomeride (*B*) by heating with acetyl chloride, whereas the reverse change—(*B*) into (*A*)—is partly accomplished when (*B*) is boiled with methyl alcohol.

(5) Hydroxy*iso*anhydrodihydrocryptopine (*A*) contains a hydroxyl group, since it yields with benzoyl chloride the hydrochloride of the corresponding benzoyl derivative,

$$C_{21}H_{22}O_4(O{\cdot}CO{\cdot}C_6H_5)N,HCl,$$

and the base (*B*) seems to behave in a similar manner.

(6) Boiling dilute sulphuric acid converts anhydrocryptopine into two hydroxy*iso*anhydrodihydrocryptopine sulphates, which, like the corresponding hydrochlorides, differ in their solubility in water and in crystalline form, but have approximately the same melting point. The sulphate (*A*) is the less readily soluble, melts at 174°, and yields with ammonia the free base, which is hydroxy-*iso*anhydrodihydrocryptopine (*A*), since, on solution in dilute hydrochloric acid, it yields the hydrochloride (*A*) melting at 227°. In a similar manner the sulphate (*B*) (m. p. 180°) yields with alkali hydroxides an amorphous base which is hydroxy*iso*anhydrodihydrocryptopine (*B*), because it is converted by hydrochloric acid into the hydrochloride (*B*) melting at 177°.

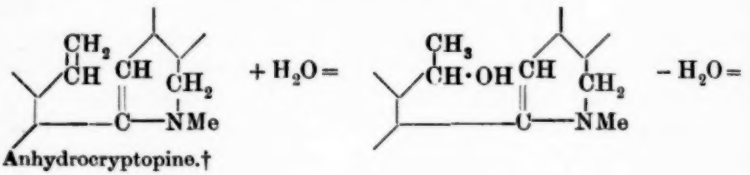
(7) Prolonged boiling with concentrated hydrochloric acid converts hydroxy*iso*anhydrodihydrocryptopine (*A*) and apparently also (*B*), $C_{21}H_{23}O_5N$, into the hydrochloride of *iso*anhydrocryptopine, $C_{21}H_{21}O_4N$, water being eliminated, and this change takes place more readily under the influence of phosphoryl chloride. *iso*Anhydrocryptopine is one of the most characteristic of the derivatives of cryptopine. It separates splendidly from methyl alcohol, melts at 158—160°, and yields sparingly soluble, beautifully crystalline salts, but, in most of its reactions it exhibits little similarity to its isomeride, anhydrocryptopine.

The facts summarised above seem to suggest that the hydroxy-*iso*anhydrodihydrocryptopines (*A*) and (*B*) are distinct isomerides, and are not merely polymorphic modifications of the same substance. When, however, the attempt is made to assign satisfactory constitutional formulæ to these bases and to form a clear picture of the processes by which anhydrocryptopine yields the hydroxy*iso*anhydrodihydrocryptopines as the result of merely boiling with dilute acids, the problem presented is obviously one of considerable complexity. The survey of all the facts leaves little doubt that, in this process, essentially one of hydration, the vinyl group must play an important part, and it is suggested that the following scheme offers an explanation of the mechanism of the reaction which is in complete harmony with the facts. When

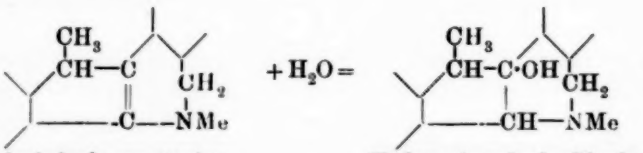
anhydrocryptopine reacts with dilute hydrochloric or sulphuric acids, it is probable that the elements of water attach themselves to the vinyl group in the first place.

The resulting intermediate product then loses water between the hydroxyl group and the reactive hydrogen atom of the CH$\ll$ group of the anhydrocryptopine molecule and *iso*anhydrocryptopine is formed.

This new substance contains, however, the same reactive unsaturated nitrogen ring as anhydrocryptopine itself, and consequently reacts further, probably at the moment of its formation,* with the boiling dilute acid with the addition of water and formation of the hydroxy*iso*anhydrodihydrocryptopines (*A*) and (*B*):



Anhydrocryptopine.†



*iso*Anhydrocryptopine. Hydroxy*iso*anhydrodihydrocryptopine (*A*) and (*B*).

It will be observed that this formula for hydroxyl*iso*anhydrodihydrocryptopine contains three asymmetric carbon atoms, and consequently affords an ample explanation for the stereoisomerism of the modifications (*A*) and (*B*). It accounts also in a simple manner for all the other known reactions of these substances; thus, for example, the formation of *iso*anhydrocryptopine by the dehydrating action of phosphoryl chloride is clearly indicated. When

* *iso*Anhydrocryptopine itself does not react readily with boiling dilute hydrochloric acid.

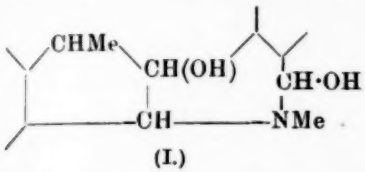
† For the purpose of this explanation it is convenient to write the formula of anhydrocryptopine in this manner, and not in the way adopted in the other sections of this paper. Examples of the addition of water to derivatives of styrene, $C_6H_5{\cdot}CH{:}CH_2$, do not appear to be frequent, but there can be no doubt that, in such cases, addition will take place in the same direction as that of the halogen acids and give derivatives of the type

$$C_6H_5{\cdot}CH(OH){\cdot}CH_3,$$

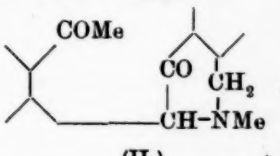
and not of the type $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. It is well known that styrene yields, with the halogen acids, α-halogen derivatives such as $C_6H_5{\cdot}CHBr{\cdot}CH_3$ and not those of the type $C_6H_5{\cdot}CH_2{\cdot}CH_2Br$.

hydroxy*iso*anhydrodihydrocryptopine (*A*) is treated with nitrous acid it does not yield a nitroso-derivative, but is converted by oxidation into dihydroxy*iso*anhydrodihydrocryptopine, $C_{21}H_{23}O_6N$, and the formation of this substance is probably due to the oxidation of the grouping $-NMe\cdot CH_2-$ to $-NMe\cdot CH(OH)-$, leading to the expression (I).

Oxidation of hydroxy*iso*anhydrodihydrocryptopine (*A*) with permanganate leads to the formation of a substance, $C_{21}H_{21}O_6N$, which is probably diketotetrahydroanhydrocryptopine (II):

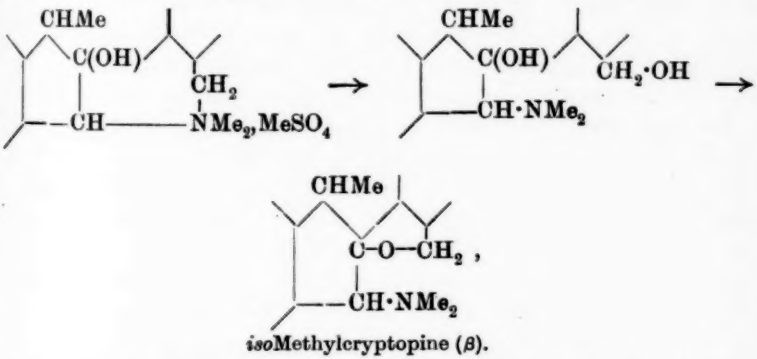


(I.)



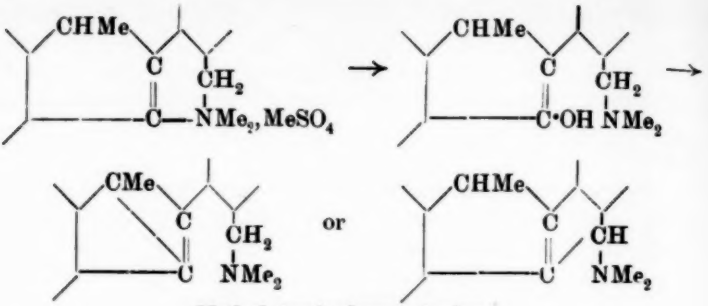
(II.)

Hydroxy*iso*anhydrodihydrocryptopine (*A*) combines readily with methyl sulphate, and the beautifully crystalline methosulphate, $C_{21}H_{23}O_5N,Me_2SO_4$, is decomposed by concentrated sodium hydroxide solution with the formation of *iso*methylcryptopine (*β*), which is a resin, but yields a well characterised iodide and platinichloride. It is suggested that the formation of *iso*methylcryptopine (*β*) is probably correctly represented by the following scheme:



*iso*Methylcryptopine (*β*).

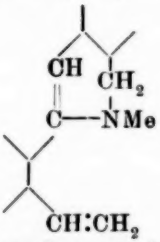
and this substance would then be closely allied in structure to methyl cryptopine (*β*) (compare p. 848). In a similar manner, *iso*anhydrocryptopine combines readily with methyl sulphate to yield the rather readily soluble, but beautifully crystalline, methosulphate, $C_{21}H_{21}O_4N,Me_2SO_4$, and this is decomposed by alkali hydroxides with the formation of methyl-*ψ*-anhydrocryptopine, $C_{22}H_{23}O_4N$, which is again a resin, but yields quite definite salts. It may be assumed that in the formation of this substance the following changes take place:



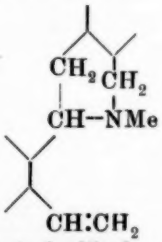
Methyl-ψ-anhydrocryptopine.

The last formula represents a structure which has some resemblance to certain of the pavine derivatives described by Pyman (T., 1915, **107**, 176). A characteristic reaction of the methosulphate of *iso*methylcryptopine (*β*), which is also shown by the methosulphate of methyl-ψ-anhydrocryptopine, is the formation of intense indigo-blue bases by the prolonged action of alcoholic potassium hydroxide (compare pp. 1000 and 1006).

In discussing the constitution of the hydroxy*iso*anhydrodihydrocryptopines (p. 862) the assumption was made that during their formation the vinyl group, $-CH{:}CH_2$, of anhydrocryptopine interacted, and was converted into the group $-CH(OH)\cdot CH_3$ by the addition of water. In order to obtain confirmatory evidence in favour of this view, the behaviour of anhydrodihydrocryptopine (*B*) (m. p. 127°, compare pp. 840, 841) towards dilute acids was carefully investigated, because this substance contains a vinyl group in the same position as that in anhydrocryptopine, but does not contain the unsaturated nitrogen ring characteristic of the latter, which, since it takes part in the formation of the hydroxy*iso*anhydrodihydrocryptopines, complicates the issue:



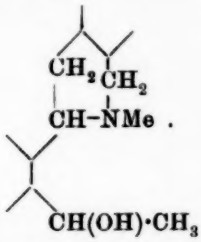
Anhydrocryptopine.



Anhydrodihydrocryptopine.

Unfortunately, this investigation was rendered difficult by the fact that the salts of anhydrodihydrocryptopine (*B*) are very sparingly soluble, and consequently resist the action of dilute acids in a remarkable degree. However, when the concentrations of dilute

sulphuric and hydrochloric acids which convert anhydrocryptopine so readily into the hydroxy*iso*anhydrodihydrocryptopine salts are employed, a small quantity of a base, $C_{21}H_{25}O_5N$, is always produced, which is derived from anhydrodihydrocryptopine (*B*) by the addition of water, and doubtless has the constitution:



This base—hydroxytetrahydroanhydrocryptopine—is amorphous, but yields a crystalline hydriodide and a characteristic platinichloride, and its formation may be taken as evidence that the vinyl group, in substances of the type of anhydrocryptopine, is capable of hydration when it is subjected to the action of boiling dilute acids.

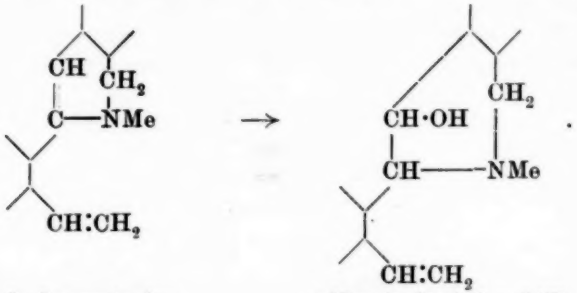
The epi*Cryptopines and* epi*Methylcryptopines.*

I. *The* epi*Cryptopines.*

Probably the most striking property of anhydrocryptopine is the brilliant crimson colour which is produced when this substance is digested with concentrated hydrochloric acid. If this solution is cooled, a very sparingly soluble salt separates, which consists of the hydrochlorides of two substances, $C_{21}H_{23}O_5N$, isomeric with cryptopine, and for reasons which are explained later, these have been named the *epi*cryptopines (*A*) and (*B*). *epi*Cryptopine (*A*) is a crystalline substance, melts at 210—212°, and closely resembles cryptopine in its physical properties, whereas *epi*cryptopine (*B*) is a colourless resin which, so far, has not been obtained in the crystalline condition. When this resin is digested with dilute hydrochloric acid, it yields *epi*cryptopine (*A*), whereas boiling with alcohol brings about the reverse change and converts *epi*cryptopine (*A*) into the resinous modification (*B*).

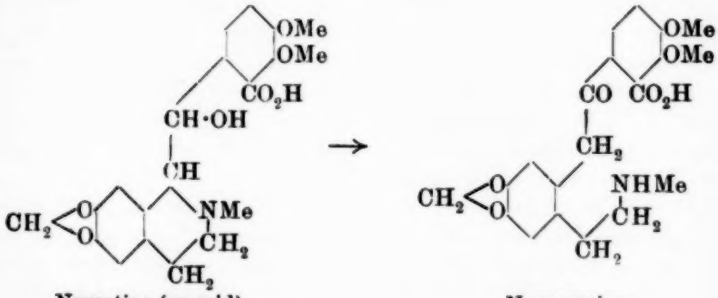
Both modifications yield very stable salts which are remarkably sparingly soluble, and both yield, on treatment with acetic anhydride, the same acetyl derivative, which melts at 285—290° and is characterised by its insolubility in ordinary solvents and by the fact that it resists hydrolysis in a remarkable degree. These *epi*cryptopines (*A*) and (*B*) are produced by the addition of the elements of water to anhydrocryptopine, and their properties suggest that they are stereoisomeric modifications of the same substance, and

that their relationship to anhydrocryptopine and formation from this substance may perhaps be indicated by the scheme:



Anhydrocryptopine. *epi*Cryptopine (*A*) and (*B*).

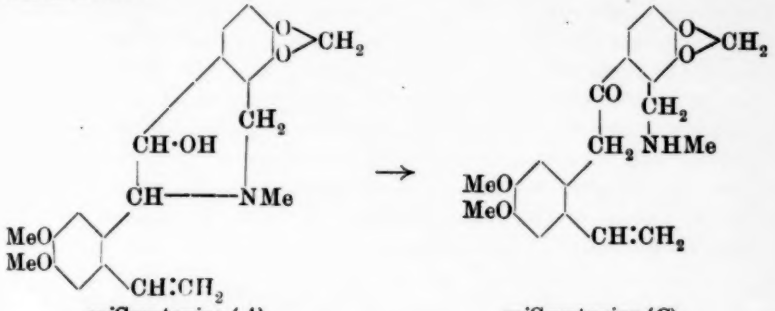
When *epi*cryptopine (*A*) is boiled with ethyl acetate it is gradually converted into the acetate of a third modification, which melts at 167° and has been named epi*cryptopine* (*C*), and the acetate of this substance is also produced when *epi*cryptopine (*A*) is digested with dilute acetic acid, but this change does not take place when dilute mineral acids are employed. A similar state of things has been observed in the case of other amino-alcohols, namely, that they are capable of isomeric change when boiled with dilute acetic acid, but not on treatment with dilute mineral acids. Thus the alkaloids cinchonine and narcotine, both of which contain the grouping –NMe·CH·CH(OH)– when boiled with dilute acetic acid, undergo molecular change in such a way that this grouping becomes –NHMe and $-CH_2\cdot CO-$. Narcotine, for example, on boiling with dilute acetic acid, yields nornarceine (Rabe, *Ber.*, 1907, **40**, 3280), a change which is better shown by representing narcotine as the hydroxy-acid rather than as the lactone:



Narcotine (as acid). Nornarceine.

If the full formula suggested for *epi*cryptopine (*A*) is compared with that of narcotine, the similarity in constitution is obvious, and it is at once seen that the change from *epi*cryptopine (*A*) to (*C*)

may well follow the same lines as the conversion of narcotine into nornarceine:

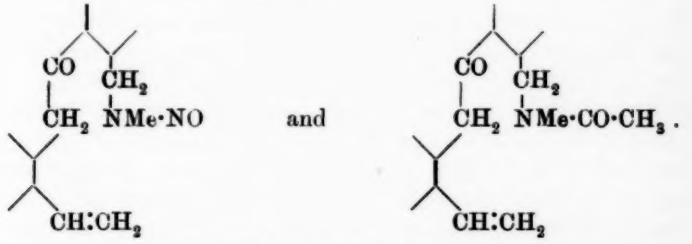


*epi*Cryptopine (*A*). *epi*Cryptopine (*C*).

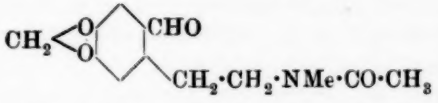
Now *epi*cryptopine (*A*) yields a nitroso-derivative,

$$C_{21}H_{22}O_5N\cdot NO,$$

and if its formula is really represented as above it follows that in the formation of the nitroso-derivative, and also of the characteristic acetyl derivative, molecular change to (*C*) must first take place, and that these derivatives are, in fact, really derived from (*C*) and contain the groupings:

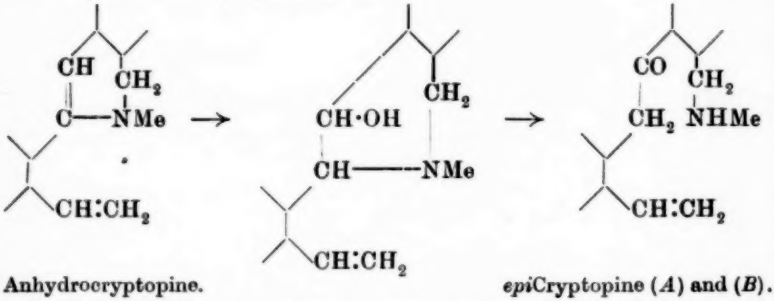


It seems quite clear that in the acetyl derivative the acetyl group is attached to nitrogen because its great stability to hydrolytic agents shows that it cannot be an OAc-derivative, and, indeed, an example of the similar stability of its acetyl derivative has been observed in the analogous case of acetylhydrastinine:



which also resists hydrolysis by acids and alkalis in a remarkable degree. Experiment has shown that *epi*cryptopine (*C*) does actually yield the same acetyl derivative as (*A*), but whereas the conversion in the case of (*A*) takes place almost instantaneously in the cold, it is necessary to boil for some time in the case of (*C*). These considerations, as well as the striking correspondence in

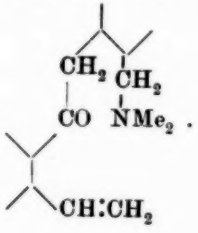
properties between *epi*cryptopine (*A*) and *epi*methylcryptopine (*A*) (see next section), seem to suggest that these two substances are similarly constituted. Since, however, *epi*methylcryptopine (*A*) must contain the group $-NMe_2$ it cannot have a formula similar to that suggested for *epi*cryptopine (*A*), but must be built up on the scheme represented for *epi*cryptopine (*C*). These considerations, as well as others which have gradually become apparent during the detailed comparison of the *epi*cryptopines with the *epi*methylcryptopines, have led irresistibly to the conclusion that the formation of the *epi*cryptopines (*A*) and (*B*) is most probably that represented by the scheme:



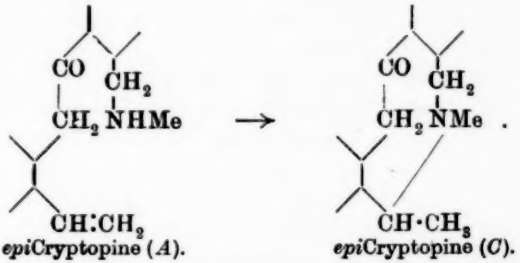
Anhydrocryptopine. *epi*Cryptopine (*A*) and (*B*).

and that the substances (*A*) and (*B*) are respectively the enol- and keto-modifications of the same formula. It will be seen that the group $-CO\cdot CH_2-$ is in the reverse position in this formula to that which it occupies in the formula of cryptopine—an interchange similar to that which exists in the cases of camphor and *epi*camphor—and it is for this reason that the name *epi*cryptopine has been adopted for the substances (*A*) and (*B*). The addition of water to the double linking in anhydrocryptopine cannot take place in the reverse direction, that is:

because, in the analogous case of the formation of the *epi*methylcryptopines (*A*) and (*B*) (compare p. 870), if a similar scheme were followed it would lead to the production of methylcryptopine (γ):



which, however, is not produced by the process under consideration. The constitution of *epi*cryptopine (*C*) may be deduced on the assumption that the narcotine-nornarceine reaction (p. 866) is reversible in this particular case and under the conditions employed. Another view which is put forward as the more probable interpretation is that the change from *epi*cryptopine (*A*) to *epi*cryptopine (*C*) takes place with the co-operation of the vinyl group, thus:



*epi*Cryptopine (*A*). *epi*Cryptopine (*C*).

This suggestion necessitates the presence of the –NHMe group, and obviously affords a simple explanation for the non-existence of an *epi*methylcryptopine (*C*), since a substance of this kind cannot be produced if, as is the case in methylcryptopine, the –NHMe group is replaced by the group $-NMe_2$. It also accounts for the facts (i) that *epi*cryptopine (*C*) does not readily yield a nitroso-derivative, and (ii) that, although it yields the same acetyl derivative as *epi*cryptopine (*A*), it does so only with difficulty, and then only incompletely. In the case of *epi*cryptopine (*A*), the –NHMe group on which both these reactions depend is ready to hand, whereas in order that the same processes may take place in the case of *epi*cryptopine (*C*) the change must be an indirect one, since it is necessary that the nine-membered ring shall first undergo fission.

The conversion of *epi*cryptopine (*A*) into *epi*cryptopirubin chloride by the action of phosphoryl chloride is described on p. 872.

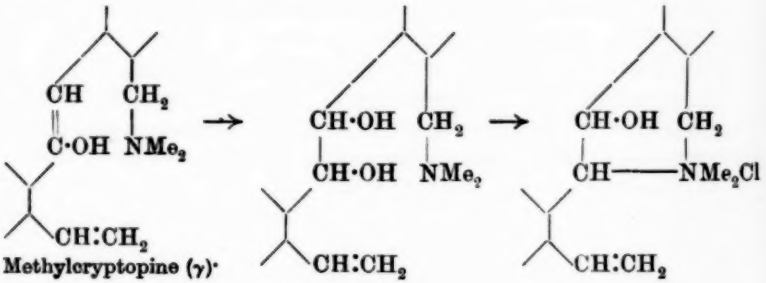
II. *The* epi*Methylcryptopines and* isoepi*Methylcryptopine.*

It was pointed out in the last section that anhydrocryptopine dissolves in boiling hydrochloric acid to a deep crimson solution, from which the sparingly soluble hydrochlorides of *epi*cryptopine (*A*) and (*B*) separate on diluting with water and cooling. The methylcryptopines (*β*) and (γ) show a somewhat similar behaviour, since they dissolve in concentrated hydrochloric acid to form colourless solutions, which, when boiled, become deep reddish-violet, and, in the case of methylcryptopine (γ), a sparingly soluble hydrochloride separates when the product is diluted and cooled (p. 1019).

Since this characteristic change seemed likely to throw light on the nature and mode of formation of the *epi*cryptopines it has been investigated so far as limited material allowed.

The sparingly soluble hydrochloride, as in the corresponding case of the hydrochloride obtained from anhydrocryptopine (p. 865), yields, with ammonia, a mixture of two epi*methylcryptopines*, of which the modification (*A*) melts at 223° and the modification (*B*) is a resin, and these two substances have many properties in common with the *epi*cryptopines (*A*) and (*B*), whilst in other respects they exhibit important differences.

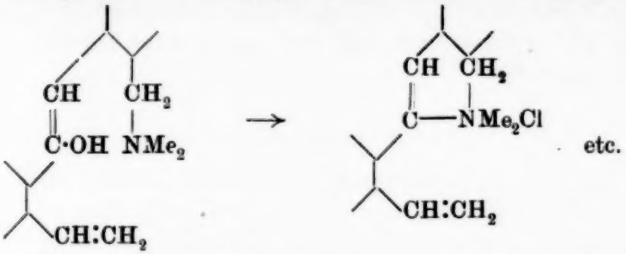
Thus *epi*methylcryptopine (*B*) is converted into (*A*) when it is digested with dilute hydrochloric acid, and the reverse change takes place when (*A*) is heated with methyl alcohol in a sealed tube, and these changes are also characteristic of the *epi*cryptopines (*A*) and (*B*). On the other hand, the *epi*methylcryptopines do not yield characteristic acetyl derivatives, and are not converted into crystalline *epi*methylcryptopirubin salts by the action of phosphoryl chloride. Furthermore, *epi*methylcryptopine (*A*) is not converted into an isomeric modification corresponding with *epi*cryptopine (*C*) when it is heated with dilute acetic acid. These facts throw considerable light on the problem of the constitution of the *epi*cryptopines and *epi*methylcryptopines and their mode of formation. It seems probable that the formation of the *epi*methylcryptopines proceeds on the following lines:



Methylcryptopine (γ).

*epi*Methylcryptopines (*A*) and (*B*).

For a long time it was thought that the alternative process:



etc.

was the correct view, but the quaternary chloride represented is the normal methochloride of anhydrocryptopine, and recent experiments (p. 982) have shown that this chloride does not yield an *epi*methylcryptopine when it is boiled with concentrated hydrochloric acid, but is decomposed with elimination of a methyl group and formation of *ψ*-cryptopine chloride.

It seems probable that the *epi*methylcryptopines thus produced, and which are, as has already been mentioned, so readily converted the one into the other, are either stereoisomeric or tautomeric modifications of the same formula. It was pointed out in discussing the *epi*cryptopines that the formation of the sparingly soluble acetyl derivative, which resists hydrolysis to so remarkable a degree, is due to the presence of the grouping $-CH_2\cdot NHMe$, and the fact that this group is replaced by $-CH_2\cdot NMe_2$ in the *epi*methylcryptopines supplies the explanation for the non-formation of a similar acetyl derivative in the case of the latter.

It is also clear that, if these formulæ are accepted, it is impossible for *epi*methylcryptopine (*A*) to yield a modification corresponding with *epi*cryptopine (*C*) by treatment with dilute acetic acid.

When methylcryptopine (γ) is boiled with concentrated hydrochloric acid the yield of the sparingly soluble *epi*methylcryptopine hydrochlorides is only small, and the main product of the action is contained in the crimson mother liquor. This on treatment with ammonia yields a resinous base, $C_{22}H_{25}O_5N$, which is isomeric with the methylcryptopines and *epi*methylcryptopines, and has provisionally been named isoepi*methylcryptopine*. This substance appears to be quite definite; it yields very soluble crimson salts, and it seems probable that its formation is due to the following changes:

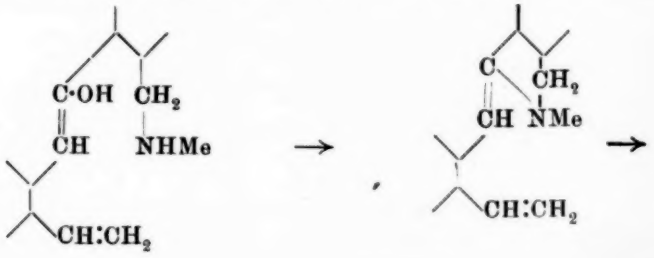
Methylcryptopine (γ : enol). *isoepi*Methylcryptopine.

A resinous base, $C_{22}H_{25}O_5N$, which may possibly be the same *isoepi*methylcryptopine, is produced when methylcryptopine (*β*) is digested with hydrochloric acid and the crimson solution decomposed by ammonia.

The epi*Cryptopirubin Salts.*

*epi*Cryptopine (*A*) undergoes a remarkable change when boiled with phosphoryl chloride, and the product, on dilution with water, yields a splendid salt, $C_{21}H_{22}O_4NCl$, which separates from water as a brilliant crimson, crystalline precipitate closely resembling mercuric iodide in appearance, and has been named epi*cryptopirubin chloride*. The corresponding iodide, $C_{21}H_{22}O_4NI$, is still more highly coloured, and the platinichloride is a deep maroon powder. It is very difficult to picture the changes that must take place in the conversion of *epi*cryptopine, which is colourless, into the intensely coloured *epi*cryptopirubin chloride, and any explanation that is put forward must be accepted as merely a tentative one. A valuable clue to the formation of *epi*cryptopirubin chloride is, however, afforded by the fact that *epi*methylcryptopine (*A*) is not converted by the action of phosphoryl chloride into a similar scarlet salt. Since then the essential difference between *epi*cryptopine (*A*) and *epi*methylcryptopine (*A*) is that the former contains the grouping –NHMe, whereas the latter has two methyl groups attached to the nitrogen atom, the resulting formula for *epi*cryptopirubin chloride must be one that can result from an *epi*cryptopine containing the –NHMe group, but not from one containing the group $-NMe_2$.

Represented as an equation, the change from *epi*cryptopine (*A*) to *epi*cryptopirubin chloride is $C_{21}H_{23}O_5N,HCl = C_{21}H_{22}O_4NCl + H_2O$, but the function of the phosphoryl chloride is evidently not only that of removing water, and it is clear that considerable rearrangement of the molecule must also take place at the same time. The most probable explanation seems to be that the vinyl group $>CH{\cdot}CH_2$ takes part in the reaction and is converted into the grouping $>CHCl{\cdot}CH_3$, which then reacts with the –NHMe group and causes rearrangement possibly according to the scheme:



*epi*Cryptopirubin chloride.

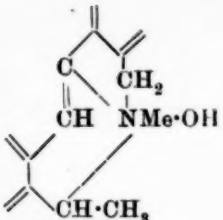
It is clear that such a change could not take place if the substance subjected to the action of phosphoryl chloride has contained two methyl groups attached to nitrogen, and the above view of the constitution of *epi*cryptopirubin chloride has other considerations in its favour.

Thus the number of conjugated double linkings, marked as heavy lines in the formula, affords an explanation for the striking colour of the salt. Again, the formula represents the salt as quaternary, and its behaviour fully bears out this view, since the aqueous solution gives no precipitate on the addition of ammonia in the cold.

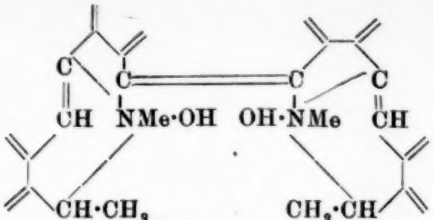
When, however, the aqueous solution of the salt is covered with ether and mixed with potassium hydroxide, the ethereal layer becomes deep green, but if shaken with air oxidation takes place, the colour changes to yellow, and a black, apparently crystalline base separates, which contains two atoms of hydrogen less than the *epi*cryptopirubin base. The whole change, which is reminiscent of the formation of the Homolka colour base (diaminofuchsonimine), may be represented thus:

$C_{21}H_{22}O_4NCl$	$C_{21}H_{22}O_4N\cdot OH$	$C_{21}H_{20}O_4N\cdot OH$.
*epi*Cryptopirubin chloride.	Green base.	Black base.

The black base has been named *dehydroepicryptopirubin hydroxide*, and yields with hydrochloric acid a purplish-red, crystalline salt which has much the same appearance as amorphous phosphorus. Owing to the intensity of its colour and of that of its salts, it seems probable that the black base is produced by the combination of two molecules of *epi*cryptopirubin hydroxide by the removal of four atoms of hydrogen from the two CH_2-groups, a change somewhat similar to the oxidation of two molecules of ψ-indoxyl to indigotin, and which would well account for the intensification of the colour:

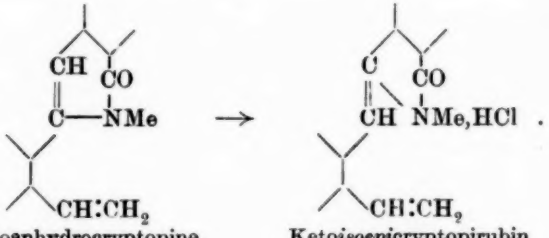


Green base.



Black base.

*Keto*isoepi*cryptopirubin Hydrochloride.*—It has been shown on p. 851 that anhydrocryptopine is readily oxidised by permanganate with the formation of ketoanhydrocryptopine, which melts at 163° and is characterised by the peculiarity, due to the proximity of the keto-group to the nitrogen atom, that, unlike anhydrocryptopine, it has very feeble basic properties, as is evidenced by the fact that the solutions of its salts in mineral acids or in acetic acid are dissociated on the addition of water with separation of the base. When this substance is boiled with phosphoryl chloride it yields a dark maroon solution, from which, on the addition of ice, a deep crimson, crystalline precipitate of *keto*isoepi*cryptopirubin hydrochloride*, $C_{21}H_{19}O_5N,HCl$, separates. The formation of this interesting and intensely coloured salt evidently takes place on somewhat different lines from that of *epi*cryptopirubin chloride from *epi*cryptopine (*A*) and phosphoryl chloride, and it does not appear likely that, in the present case, the vinyl group takes part in the change. Possibly the conversion may be represented thus:



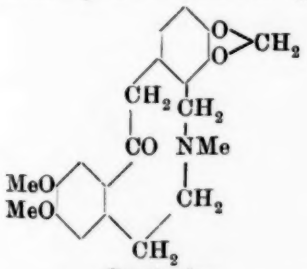
Ketoanhydrocryptopine. Keto*isoepi*cryptopirubin hydrochloride.

Like ketoanhydrocryptopine hydrochloride, with which it is isomeric, the ketorubin salt is readily dissociated when it is boiled with water into hydrochloric acid and the *keto*isoepi*cryptopirubin base*, $C_{21}H_{19}O_5N$, which separates from dilute acetic acid in brilliant prisms and melts indefinitely at about 235—240°. This base is insoluble in dilute hydrochloric acid, but dissolves in the concentrated acid to a deep crimson solution, which doubtless contains the original keto*isoepi*cryptopirubin hydrochloride.

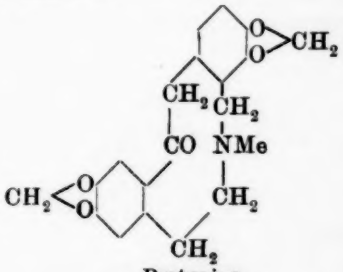
Protopine, $C_{20}H_{19}O_5N$.

Protopine, also called fumarine or macleyine, one of the most widely distributed of the alkaloids, occurs in all the *Papaveraceae*, in the roots of *Chelidonium majus*, *Macleya cordata*, and *Sanguinaria canadensis*, in *Corydalis cava*, and in many other plants, but almost always in very small quantity. It was discovered by O. Hesse (*Annalen*, *Suppl.*, 1872, **8**, 261) in opium, and is found, along with cryptopine, in the filtrate after the morphine and thebaine have been separated, but its purification, and especially its complete separation from cryptopine, is a tedious and difficult matter. Probably the most convenient source of protopine is the root of *Dicentra spectabilis*, in which it occurs to the extent of 0·7—1·0 per cent., and from which it may be extracted by alcohol and readily purified (compare Gadamer, *Chem. Zentr.*, 1901, II., 814; Danckwortt, *Habilitations Schrift*, Breslau, 1912, p. 25).

Protopine crystallises in monoclinic prisms, melts at 207°, and exhibits in all its properties the most striking resemblance to cryptopine, from which, however, it differs in that it does not contain methoxy-groups, although, like cryptopine, it contains a methyl group attached to nitrogen. The formula of protopine, $C_{20}H_{19}O_5N$, contains CH_4 less than that of cryptopine, $C_{21}H_{23}O_5N$, and it has been suggested by Gadamer and Danckwortt that these alkaloids are similarly constituted, and differ only in the replacement of the 2MeO in cryptopine by the methylenedioxy-group, $CH_2{:}O_2$. During the course of the present research a careful comparison between cryptopine and protopine has been made, and it has been shown that certain highly characteristic changes which cryptopine has been found to undergo are exhibited in a precisely similar manner by protopine, so there can no longer be any doubt that these alkaloids are intimately connected, and their relationship is obviously that exhibited by the formulæ:



Cryptopine.

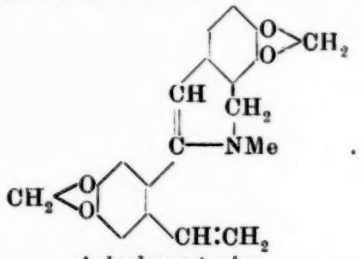


Protopine.

Protopine is converted by the action of phosphoryl chloride into iso*protopine chloride*, $C_{20}H_{18}O_4NCl$, and yields, when digested with sulphuric acid in acetic acid solution, the highly characteristic

disulphate, $C_{20}H_{18}O_4N,HSO_4,H_2SO_4$, and these salts have properties which are almost identical with those of the corresponding *iso*cryptopine salts (pp. 834 and 884).

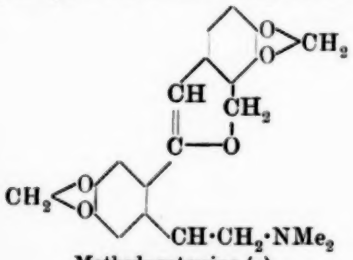
One of the most striking properties of cryptopine is the conversion of *iso*cryptopine chloride, $C_{21}H_{22}O_4NCl$, into anhydrocryptopine (m. p. 110°), $C_{21}H_{21}O_4N$, by the action of methyl-alcoholic potassium hydroxide, and *iso*protopine chloride exhibits an exactly similar behaviour, and yields *anhydroprotopine*, $C_{20}H_{17}O_4N$, which melts at 114°. Furthermore, anhydroprotopine behaves towards boiling concentrated hydrochloric acid precisely in the same way as does anhydrocryptopine; the solution becomes red and deposits a slimy hydrochloride, which is evidently *epi*protopine hydrochloride (compare *epi*cryptopine, p. 865). It is clear, therefore, that if the constitution assigned to anhydrocryptopine (p. 850) is accepted, the constitution of anhydroprotopine must be written as follows:



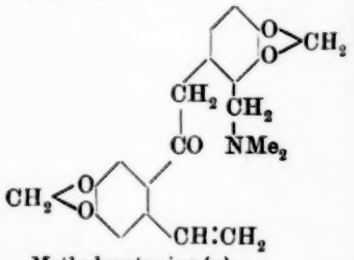
Anhydroprotopine.

Like cryptopine, protopine combines readily with methyl sulphate, and the *methosulphate*, $C_{20}H_{19}O_5N\cdot Me_2SO_4$, is decomposed by methyl-alcoholic potassium hydroxide, yielding two *methylprotopines*, (β) and (γ), which melt at 145° and 112°, and correspond in all their properties with the two methylcryptopines, (α) and (γ) (p. 845), melting at 153° and 110° respectively.

There can be little doubt that the constitutions of these methylprotopines are those represented by the formulæ:



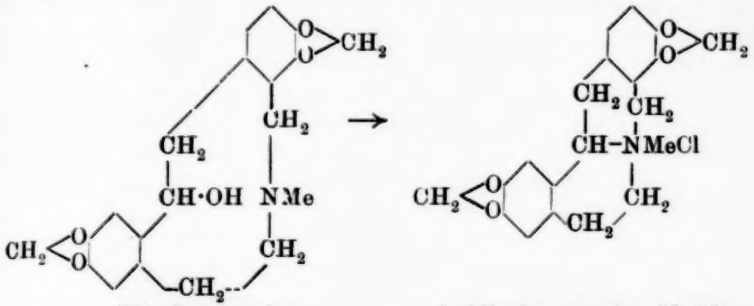
Methylprotopine (α).



Methylprotopine (γ)

Danckwortt (*loc. cit.*, p. 33) has shown that protopine is reduced when its solution in dilute sulphuric acid is boiled with sodium amalgam, yielding *dihydroprotopine*, $C_{20}H_{21}O_5N$, and this substance

is converted into the quaternary *isodihydroprotopine chloride*, $C_{20}H_{20}O_4NCl$, by the action of benzoyl chloride:



Dihydroprotopine. *iso*Dihydroprotopine chloride.

These changes find their exact counterpart in the reduction of cryptopine, under the same conditions, to dihydrocryptopine, and the subsequent conversion of the base into quaternary *iso*dihydrocryptopine chloride by the action of phosphoryl chloride (compare p. 840). It may be safely predicted, so soon as a sufficient supply of protopine is available, that this interesting alkaloid will be found to undergo all the other changes described in this communication as characteristic of cryptopine.

Experimental.

Section II.

Cryptopine and its Salts.

The formula $C_{21}H_{23}O_5N$ has been assigned to cryptopine by Hesse (*Annalen, Suppl.*, 1872, **8**, 299; compare T. and H. Smith, *Jahresber.*, 1867, 523, and Pictet and Kramers, *Ber.*, 1910, **43**, 1332) and several analyses made, in connexion with the present investigation, with different preparations of the alkaloid have confirmed this view, the mean of five such analyses yielding C = 68·2; H = 6·3; N = 3·9, whereas $C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent. Determinations of the methoxy-groups carried out by the Perkin modification of the Zeisel method (T., 1903, **83**, 1367) gave as the mean of three closely agreeing results, MeO = 16·7, whereas $C_{21}H_{23}O_5N$, containing two methoxy-groups, requires MeO = 16·8 per cent. Cryptopine melts at 218—219°, and one of its chief characteristics is its sparing solubility in all the ordinary organic solvents (compare Pictet and Kramers, *loc. cit.*, p. 1332), but it dissolves in much boiling methyl ethyl ketone or *iso*amyl alcohol, and separates on cooling in glistening prisms. It dissolves readily in hot acetophenone, and separates on keeping in hatchet-head shaped prisms, but it must not be boiled with acetophenone, otherwise decomposition with the production of a brown solution

occurs. Cryptopine is remarkably readily soluble in boiling pyridine, but much less so in the cold, and separates in hard crusts; when the concentrated solution in hot pyridine is mixed with two volumes of boiling alcohol, the cryptopine separates well and almost completely in colourless masses of ill-defined prisms, and this mixture of solvents is perhaps the most suitable medium for the purification of the alkaloid. Cryptopine exhibits a characteristic colour reaction with sulphuric acid, which is best shown by dissolving a trace of the alkaloid in one or two drops of glacial acetic acid and then adding a considerable quantity of concentrated sulphuric acid, when a pink solution is obtained, which rapidly becomes an intense bluish-violet. The behaviour of a solution of cryptopine in concentrated sulphuric acid towards gallic acid and phloroglucinol has been described by Pictet and Kramers (*loc. cit.*, pp. 1334 and 1335), who also give a table showing all the colour reactions of cryptopine.

Several of the salts of cryptopine have already been described by Hesse, Pictet, and Kramers, and others, and one of the striking properties of the alkaloid is the formation of curious gelatinous precipitates when it is dissolved in acids. Thus cryptopine dissolves readily in dilute nitric acid, and almost immediately a gelatinous mass separates, which completely fills the liquid. When, however, the solution is warmed and vigorously stirred, the *nitrate* becomes crystalline, and is obtained, by recrystallisation from very dilute nitric acid, in colourless groups of needles. In contact with porous porcelain it dries to a semi-transparent, horny mass which decomposes at about 115° with effervescence:

0·2694 gave 15·1 c.c. N_2 at 13° and 762 mm. N = 6·6.

$C_{21}H_{23}O_5N,HNO_3$ requires N = 6·6 per cent.

Cryptopine also dissolves readily in warm dilute hydrochloric acid, and the solution often remains clear for a considerable time and then sets to a voluminous mass, which consists of microscopic groups of feathery crystals. This hydrochloride dries to a brittle crust on porous porcelain, becomes powdery in the steam-oven, and melts and decomposes at about 235° with evolution of gas and formation of a syrup. The *hydriodide* is precipitated as a jelly when potassium iodide is added to the warm dilute solution of the hydrochloride, but on boiling and stirring, the salt separates in characteristic, well-defined, short prisms. It is very sparingly soluble even in boiling water, and is a stable salt since it is only very slowly discoloured at 200°, at about 225° it becomes, however, dark red, and decomposes with effervescence at about 235—240° to a red froth which soon becomes black:

0·3011 gave 0·1388 AgI. I = 24·9.

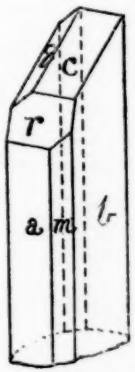
$C_{21}H_{23}O_5N,HI$ requires I = 25·5 per cent.

Perhaps the most characteristic salt of cryptopine is the *oxalate*, $C_{21}H_{23}O_5N,C_2H_2O_4$, which has been found to be most useful in purifying cryptopine from admixture with other alkaloids or impurities generally. It is obtained by dissolving cryptopine in excess of boiling dilute oxalic acid and immediately filtering, when the solution in a short time deposits glistening, prismatic needles which are very sparingly soluble in water.

Sometimes the oxalate separates as a voluminous mass like asbestos threads and, on keeping for several days, this modification becomes partly converted into large, well-developed, brilliant prisms which contain $4H_2O$, as the following analysis shows: 1·7579 lost, over phosphoric oxide, 0·2454 or 13·9, and 0·1097 of the anhydrous salt gave 0·2450 CO_2 and 0·0578 H_2O. C=60·8; H=5·8. $C_{21}H_{23}O_5N,C_2H_2O_4,4H_2O$ contains 13·6 H_2O per cent., and in the anhydrous salt, C=60·1; H=5·4 per cent. Mr. T. V. Barker has kindly measured some of these crystals, and reports as follows:

The substance is anorthic. The habit of the crystals is shown in Fig. 1, the forms being $b\{010\}$, $m\{110\}$, $a\{100\}$, $c\{001\}$, $r\{101\}$,

1



Cryptopine oxalate

and $q\{0\bar{1}1\}$. The axial ratios $a:b:c=0·5304:1:0·7569$, $\alpha=98°2'$, $\beta=112°14'$, $\gamma=85°23'$ were computed from the following measurements:

	ϕ.		ρ.	
Face.	Mean obs.	Calc.	Mean obs.	Calc.
b (010)	0°0′	0°0′	90°0′	90°0′
m (110)	*64 58	—	90 0	90 0
a (100)	*91 40	—	90 0	90 0
c (001)	75 0	72 27	*23 12	—
r (101)	87 36	87 31	62 47	62 52
q (0$\bar{1}$1)	*147 15	—	*37 4	—

There is a good cleavage parallel to $b(010)$. The crystals possess an enormous double refraction and exhibit the following extinctions: on $b(010)$, an angle of 23° with the edge ba; on $m(110)$, an angle of 6° with the edge ma; on $c(001)$, an angle of 45° with the edge cb. In convergent light an optic axis is visible through m and another through c.

Cryptopine Methosulphate, $C_{21}H_{23}O_5N,Me_2SO_4$.—This substance has usually been prepared by thoroughly mixing cryptopine (10 grams) with methyl sulphate (12 grams), and, after an hour, heating the paste on the steam-bath for an hour and mixing the syrup with an equal volume of methyl alcohol. Crystallisation soon commences, and next morning the product is collected, well washed with methyl alcohol, and recrystallised from this solvent. The brown mother liquors on exposure to the air gradually deposit a mixture of the methosulphate, cryptopine sulphate, and apparently also the methyl hydrogen sulphate; this is collected, drained on porous porcelain, and after the methosulphate has been separated by crystallisation from methyl alcohol or water the very crude cryptopine is precipitated by ammonia and purified by means of the oxalate. Cryptopine methosulphate separates very readily from methyl alcohol, in which it is sparingly soluble in the cold, in groups of glistening, prismatic needles which become chalky on keeping on porous porcelain exposed to air and very rapidly so in the steam-oven. It is readily soluble in hot water (5 grams dissolve easily in 20 c.c. of water at 50°), but much less so in the cold, and separates as a voluminous mass of long, slender needles which evidently contain water of crystallisation. When rapidly heated in a capillary tube it softens somewhat at 225° and melts at 235—238° apparently with very little decomposition. After crystallising from methyl alcohol and drying by exposure to air, the methosulphate appears still to contain 1MeOH:

0·9272 (air-dried) lost 0·0688 at 100° or 7·4 per cent., and 0·4411 of the remainder gave 0·2146 $BaSO_4$. S = 6·7.

$C_{21}H_{23}O_5N,Me_2SO_4,MeOH$ contains MeOH = 6·1 and the dry salt contains S = 6·5 per cent.

Cryptopine Methiodide, $C_{21}H_{23}O_5N,MeI$.—This fine salt was prepared by two methods, namely, (i) from cryptopine by the action of methyl iodide, and (ii) from cryptopine methosulphate by precipitation with potassium iodide. (i) A mixture of cryptopine (5 grams), methyl iodide (10 c.c.), and methyl alcohol (20 c.c.) was heated in a sealed tube in the water-bath, with frequent shaking, for two days. The yellow, crystalline cake, on the surface of which were red crystals, consisting probably of the periodide, was collected, washed with methyl alcohol, and crystallised from a large

quantity of this solvent, in which it is very sparingly soluble and from which it separates as a granular precipitate consisting of very pale yellow laminæ or small, flat prisms. (ii) The solution of cryptopine methosulphate in hot water was mixed with excess of potassium iodide, when a milky liquid was produced which soon began to crystallise. After collecting and washing with hot water the salt is almost pure, but it may be recrystallised from methyl alcohol or from hot water, in which it is very sparingly soluble and from which it separates in well-defined prisms:

0·1175 gave 0·2217 CO_2 and 0·0529 H_2O. C = 51·4; H = 5·0.
0·1512 „ 0·0701 AgI. I = 24·4.
$C_{21}H_{23}O_5N$,MeI requires C = 51·6; H = 5·1; I = 24·8 per cent.

Cryptopine methiodide softens at 210° and melts and decomposes at 215—217° to an orange mass.

Cryptopine Methochloride, $C_{21}H_{23}O_5N$,MeCl.—In order to prepare this substance the methiodide (1 gram) was ground to a fine paste with much water and heated with the silver chloride from 1 gram of silver nitrate first on the water-bath for one hour and then to boiling for a few minutes. After filtering and concentrating considerably, the methochloride separated as an apparently gelatinous mass which, however, consisted of almost colourless, microscopic crystals:

0·4097 gave 0·1326 AgCl. Cl = 8·0.
$C_{21}H_{23}O_5N$,MeCl requires Cl = 8·4 per cent.

Cryptopine methochloride is very readily soluble in boiling water, but much less so in the cold, and the cold solution is not decomposed on the addition of *N*-sodium hydroxide. When, however, the hot concentrated solution is boiled with 20 per cent. sodium hydroxide the liquid clouds and an oil separates which gradually solidifies. This crystallises from ether in colourless, glistening prisms which melt at 111° and consist of methylcryptopine (γ, p. 966).

Attempt to Resolve Cryptopine into Active Modifications.

The first experiments made in this direction were with cryptopine hydrogen tartrate. The alkaloid (2 grams) was dissolved in a hot dilute solution of tartaric acid (1 gram) and the whole allowed to cool slowly, when the tartrate separated as a gelatinous mass, and after remaining for several days in the ice-chest the jelly gave place to nodular masses consisting of small, prismatic needles. Hesse (*loc. cit.*), who first prepared this salt, states that it has the formula $C_{21}H_{23}O_5N,C_4H_6O_6,4H_2O$, and is soluble in 167 parts of water at 10° and very readily so in hot water or alcohol.

The specimen prepared as described above also contained water of crystallisation, which was not determined, but the salt, after drying at 100°, was analysed, and yielded C=57·3; H=5·8, whereas the formula $C_{21}H_{23}O_5N,C_4H_6O_6$ requires C=57·7; H=5·6 per cent. This salt, like so many of the other salts of cryptopine, does not crystallise readily, but it was five times carefully recrystallised, and the small amount remaining (0·22 gram) was dissolved in water and precipitated with ammonia. The base, which separated as a chalky powder, was dissolved in a little dilute acetic acid, and gave a solution which was quite inactive; it melted at 217—218°, and was evidently ordinary cryptopine.

The next series of experiments was made with cryptopine β-bromocamphorsulphonate, but this salt also is unfortunately not well characterised, and crystallises with difficulty. Cryptopine (2 grams) was dissolved in a hot solution of β-bromocamphorsulphonic acid and the solution allowed to cool slowly, when it clouded, and the salt separated as a syrup which in the ice-chest crystallised overnight and the supernatant liquid became filled with a jelly. The crystalline mass was collected, dissolved in much hot water, the solution then cooled with ice and vigorously stirred mechanically, when the salt separated in curious, nodular masses:

0·3041 gave 0·0837 AgBr. Br=11·7.
0·2694 „ 0·0941 $BaSO_4$. S=4·8.
0·4515 „ 7·7 c.c. N_2 at 10·8° and 760 mm. N=2·0.

$C_{21}H_{23}O_5N,C_{10}H_{15}O_4SBr$ requires Br=11·7; S=4·7; N=2·1 per cent.

This salt was recrystallised five times in the same manner, when the observed rotations in aqueous solution (concentration in all cases about 1·5 per cent.) were α_D +37·8°, 38·2°, 38·7°, 40·2°, and 40·8°.

The salt of rotation 40·8°, dissolved in water and precipitated with ammonia, yielded a chalky base which in dilute acetic acid solution was quite inactive and melted at 217—218°. In a subsequent experiment carried out with 5 grams of cryptopine, the β-bromocamphorsulphonate was five times recrystallised from acetic ester, in which it is very sparingly soluble and from which it separates as a mass of woolly needles, becoming soft at 180° and melting at 190—195° to a viscid syrup. The aqueous solution of this salt had α_D +40·1, and the base obtained by precipitating with ammonia was inactive. In a third series of experiments the salt was recrystallised seven times from a mixture of ethyl acetate (5 parts) and alcohol (1 part), in which it is more readily soluble than in ethyl acetate alone. The resulting beautifully crystalline salt had α_D +40·3 in aqueous solution, and on precipitating with ammonia

an inactive base resulted which melted at 217—218° and was obviously ordinary cryptopine.

The Quaternary Salts of iso*Cryptopine.*

A mixture of cryptopine (2 grams) and acetyl chloride (10 c.c.) gradually becomes warm, most of the alkaloid dissolves, the whole soon sets to a crystalline mass, and the reaction is completed by heating on the steam-bath for a quarter of an hour. The reflux condenser is removed, the excess of acetyl chloride distilled off, and the dry cake dissolved in boiling water, in which it is sparingly soluble, when on cooling a voluminous, satiny, crystalline mass separates, and after recrystallisation consists of pure iso*cryptopine chloride.* In preparing larger quantities of this quaternary salt by this process it was found that the fact that the cryptopine did not completely dissolve in the acetyl chloride before the separation of the *iso*cryptopine chloride commenced had as the result that this salt was apt to be contaminated with cryptopine hydrochloride often to a considerable extent, and consequently the aqueous solution of the product gave a precipitate of alkaloid on the addition of ammonia instead of remaining clear. As the separation of the two salts by fractional crystallisation from water was difficult, the above process, although the more convenient, was abandoned in favour of the following. *Preparation of* iso*Cryptopine Chloride.*—In a flask fitted with a ground-in air condenser, cryptopine (10 grams) is mixed with freshly distilled phosphoryl chloride (20 c.c.) and allowed to remain for ten minutes, during which some rise of temperature takes place, most of the cryptopine passes into solution, and the remainder dissolves when the flask is heated in an oil-bath just to boiling for forty-five minutes. After distilling off the excess of phosphoryl chloride from a steam-bath under diminished pressure, the solid residue is crystallised from boiling water and then recrystallised from 2 per cent. hydrochloric acid, drained on porous porcelain, and dried in the steam-oven, care being taken to exclude light as far as possible:

0·2799 gave 0·0979 AgCl. Cl = 8·7.

$C_{21}H_{22}O_4NCl$ requires Cl = 9·2 per cent.

iso*Cryptopine chloride* becomes somewhat yellow at 130°, darkens considerably between 210° and 220°, and melts and decomposes at about 223° to a dark brown froth; it is sparingly soluble in cold water, not very readily so in boiling, and the solution gives no precipitate on the addition of ammonia. A trace of the salt, dissolved in hot very dilute sulphuric acid, gives on the addition of manganese dioxide an intense purple coloration which on boiling becomes brown.

The *platinichloride* separates on the addition of platinic chloride to a solution of the chloride in warm very dilute hydrochloric acid as a very finely divided, pale yellow, crystalline precipitate which is difficult to filter:

0·1153 gave 0·1909 CO_2 and 0·0417 H_2O. C = 45·2; H = 4·0.
0·2999 „ 0·0525 Pt. Pt = 17·5.
$(C_{21}H_{22}O_4N)_2PtCl_6$ requires C = 45·3; H = 4·0; Pt = 17·5 per cent.

The *aurichloride* is obtained as a drab purple precipitate when auric chloride is added to the solution of the chloride in dilute hydrochloric acid:

0·1400 gave 0·1858 CO_2 and 0·0416 H_2O. C = 36·2; H = 3·3.
0·9696 „ 0·2778 Au. Au = 28·6.
$C_{21}H_{22}O_4N,AuCl_4$ requires C = 36·4; H = 3·2; Au = 28·5 per cent.

The *iodide* is precipitated on the addition of potassium iodide to the warm aqueous solution of the chloride as a heavy, white granular precipitate, which, after collecting, washing with hot water, and drying in the steam-oven, gave the following results on analysis:

0·1105 gave 0·2144 CO_2 and 0·0488 H_2O. C = 52·9; H = 4·9.
$C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·6 per cent.

iso*Cryptopine iodide* dissolves appreciably, although sparingly, in boiling water, and separates on cooling as a granular, crystalline meal.

When rapidly heated in a capillary tube, it becomes bright yellow between 150° and 170°, orange between 170° and 190°, then rapidly much darker, and melts at about 245—247° with effervescence to a bright crimson resin. It becomes discoloured when exposed to light.

iso*Cryptopine Disulphate*, $C_{21}H_{22}O_4N,HSO_4,H_2SO_4$.—This curious and beautiful salt is obtained in a good yield by the action of a mixture of sulphuric acid and acetic acid on cryptopine. Cryptopine (1 gram) is mixed with glacial acetic acid (10 c.c.) and sulphuric acid (1 c.c.) and heated on a rapidly boiling water-bath, when the whole dissolves at first but, after some time, crystals begin to separate from the hot liquid. The heating is continued during two hours, the pasty mass set aside overnight, and the crystalline precipitate collected and washed with glacial acetic acid. The salt is then almost pure, but may be recrystallised by dissolving in much boiling water, when, on keeping, the whole sets to a voluminous mass of crystals which are collected and drained on porous porcelain in the dark, because the salt rapidly turns blue when exposed to light. The yield is about 1·1 grams, and a further small quantity separates from the mother liquors on long keeping in the ice-chest:

0·1804 gave 0·3039 CO_2 and 0·0850 H_2O. C = 45·9; H = 5·2.
0·3225 „ 0·2621 $BaSO_4$. S = 11·2.

$C_{21}H_{22}O_4N,HSO_4,H_2SO_4$ requires C = 46·1; H = 4·6; S = 11·7 per cent.

iso*Cryptopine disulphate* is a very stable substance; it is scarcely discoloured at 200°, is slightly ochreous at 230°, darkens considerably at 230—245°, and decomposes at 250° with evolution of much gas and formation of a brown froth which rapidly becomes black. It dissolves in concentrated sulphuric acid with a splendid reddish-violet colour which gradually becomes bluish-violet, and on carefully warming in hot water the colour becomes indigo-blue and then bluish-black. The solution in water gives on the addition of manganese dioxide an intense purple colour, especially on boiling. The most striking property of the disulphate is its susceptibility to light. If a trace of the moist salt is rubbed with the finger across a polished piece of black wood a highly characteristic pale blue streak is produced and filter-paper saturated with the aqueous solution of the salt becomes sky-blue when it is exposed to sunlight.

When the aqueous solution of the disulphate is mixed with dilute nitric acid and heated on the steam-bath it becomes an intense blue, then deep green, and then brown, and a bluish-green precipitate separates; if the heating is continued, rapid oxidation sets in and a crystalline, orange substance separates in quantity, which was not further examined. The addition of concentrated hydrochloric acid to a hot saturated solution of the disulphate causes the immediate separation of a colourless, crystalline precipitate, and this was collected, washed with dilute hydrochloric acid, in which it is very sparingly soluble, drained on porous porcelain in the dark, and dried over phosphoric oxide. It then appeared to consist mainly of a dichloride, since it contained Cl = 14·5 ($C_{21}H_{22}O_4NCl,HCl$ contains Cl = 16·7 and $C_{21}H_{22}O_4NCl$ contains Cl = 9·2 per cent.). When this salt was recrystallised from water several times the percentage of chlorine was found to be 9·14, and the salt was then apparently *iso*cryptopine chloride (p. 883). Since it seemed interesting to ascertain what salt would be produced by the double decomposition of the disulphate with potassium iodide, this reagent was added in large excess to the hot solution of the disulphate, causing the immediate precipitation of a voluminous, crystalline salt. On analysis this salt gave C = 52·2; H = 4·8, whereas $C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·6 per cent., and a careful comparison showed that the salt was *iso*cryptopine iodide (p. 884). When a hot aqueous solution of the disulphate (5 grams) was treated with exactly sufficient barium hydroxide to remove the sulphuric acid, a pale yellow, very strongly alkaline solution was obtained, and when this was

concentrated to 50 c.c. by distillation under diminished pressure from the steam-bath it set to a jelly which could not be filtered and was almost insoluble in ether. This jelly is probably iso*cryptopine*, since it yields with sulphuric, hydrochloric, and hydriodic acids the corresponding salts of *iso*cryptopine.

iso*Cryptopine Sulphate*, $(C_{21}H_{22}O_4N)_2SO_4$.—If a hot concentrated aqueous solution of the disulphate is mixed with a large excess of concentrated ammonia the colour changes to yellow, and, on keeping, an almost colourless, very voluminous, glistening precipitate separates which resembles the "silver salt" of the alizarin manufacturer. This was collected, washed, and recrystallised from dilute ammonia:

0·1015 gave 0·2325 CO_2 and 0·0514 H_2O. C = 62·4; H = 5·5.
0·4654 „ 11 c.c. N_2 at 18° and 760 mm. N = 2·9.
0·3280 „ 0·0898 $BaSO_4$. S = 3·8.

$(C_{21}H_{22}O_4N)_2SO_4$ requires C = 63·0; H = 5·5; N = 3·0; S = 4·0 per cent.

This silvery modification of the sulphate begins to darken at about 140°, becomes orange at about 150°, gradually gets darker, shrinks at 185—190°, is nearly black at 200°, and melts to a black tar at 215—220°.

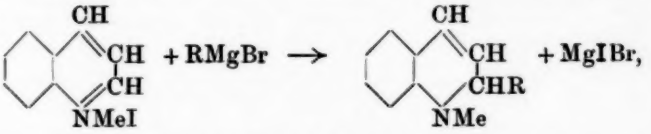
It develops a remarkable blue colour when exposed to light, and especially when moistened with alcohol and rubbed in a thin layer on a polished black surface. It is very sparingly soluble in water, but dissolves readily in boiling methyl alcohol (10 grams readily in 50 c.c.), and on cooling immediately the satiny modification soluble in methyl alcohol separates, but when the whole is left a remarkable change takes place and the voluminous, silvery mass gradually becomes filled with heavy, orange, prismatic crystals which are very sparingly soluble in methyl alcohol, and this change continues during several days and apparently does not proceed to completion. In order to obtain the orange crystals from the unchanged satiny mass it is only necessary to warm gently, when the former readily dissolve and the latter remains.

The decanted liquid on keeping gradually undergoes the same slow transformation. The orange prisms rapidly become opaque when exposed to air, and the loss on exposure over phosphoric oxide in a vacuum and then at 100° was in one case as much as 21·4 per cent., corresponding roughly with $(C_{21}H_{22}O_4N)_2SO_4$,7MeOH, which requires MeOH = 21·8 per cent.

Analysis showed that the anhydrous salt has the same composition as the original silvery modification (Found, C = 62·5; H = 5·5; S = 4·1 per cent.), and the two salts are therefore obviously polymorphic modifications of the same substance.

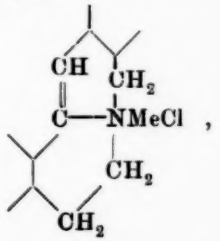
Action of the Grignard Reagent on iso*Cryptopine Chloride.*

The action of magnesium alkyl haloids on quinoline and *iso*quinoline derivatives has been very fully investigated by Freund and his co-workers, especially in connexion with derivatives of cotarnine and berberine (compare *Ber.*, 1904, **37**, 3336, 4673; 1907, **40**, 2604, and especially *Annalen*, 1913, **397**, 30). Freund showed that 1:2-dihydro*iso*quinoline derivatives, for example, yield with the Grignard reagent alkyl derivatives, the reagent acting at the double linking between the nitrogen atom and the α-carbon atom in such a way that the new alkyl group becomes attached to the α-carbon atom:



In the case of berberine chloride action takes place in accordance with the scheme:

The formula for *iso*cryptopine chloride:

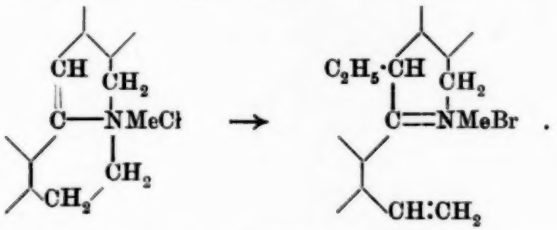


does not contain a double linking between the nitrogen and the neighbouring carbon atoms, and it seemed therefore interesting to determine whether this substance would react with the Grignard reagent, and this appears to be the case. When the finely divided and carefully dried chloride (1 gram) was digested with ethyl bromide (1 gram), magnesium (0·2 gram), and ether (6 c.c.) for ten hours, a heavy salmon-coloured mass was obtained, which was collected, washed with ether and then with dilute hydrobromic acid, and crystallised from water, in which it is very sparingly soluble, and from which it separates as a voluminous mass of satiny needles:

0·3335 gave 8·5 c.c. N_2 at 10° and 764 mm. N = 3·0.
0·2345 „ 0·0960 AgBr. Br = 17·4.
$C_{23}H_{26}O_4NBr$ requires N = 3·0; H = 17·4 per cent.

Ethyldihydroisoanhydrocryptopine bromide darkens at 220° and melts at 227° to a dark brown mass; it is sparingly soluble in boiling alcohol, and separates on cooling as a chalky mass consisting of minute prisms. The corresponding iodide was readily obtained when *iso*cryptopine chloride was digested in a reflux apparatus with an ethereal solution of magnesium ethyl iodide. After collecting and washing with dilute hydriodic acid the mass was boiled with much alcohol, in which it is very sparingly soluble, when the filtered solution deposited along with other substances a red, ochreous, crystalline mass melting and decomposing at 228—230°, evidently consisting of *ethyldihydroisoanhydrocryptopine iodide*. (Found, C = 53·9; H = 4·7. $C_{23}H_{26}O_4NI$ requires C = 54·4; H = 5·1 per cent.). It is probable that these substances, which have so far not been further investigated, but appear to be quaternary salts, are produced according to the scheme below.

Since the unsaturated *α*-position in relation to the nitrogen atom is not available, the ethyl group of the magnesium ethyl bromide, for example, probably attaches itself to the reactive =CH– group, and the formation of ethyldihydro*iso*anhydrocryptopine bromide will then occur in the following manner:



It is hoped on a future occasion to investigate more fully this interesting interaction.

Oxidation of Cryptopine with Permanganate.

Formation of 6:7-*Dimethoxy-2-methyltetrahydro*isoquinolone,

$$(MeO)_2C_6H_2\begin{cases}CO—NMe\\ CH_2\cdot CH_2\end{cases}$$

and m-*Hemipinic Acid*, $(MeO)_2C_6H_2(CO_2H)_2$.

Cryptopine itself is scarcely attacked by permanganate under ordinary conditions and only with difficulty at the temperature of the steam-bath, and the best results were obtained by using a nearly neutral solution of the hydrochloride, but even then the

yield of product was very small, and much cryptopine remained unattacked. Cryptopine (15 grams), dissolved in rather more than the theoretical quantity of very dilute hydrochloric acid (500 c.c.), was heated on the steam-bath in a flask fitted with a mechanical stirrer and oxidised by the addition, drop by drop, of potassium permanganate (100 grams) in hot water (1500 c.c.), a rapid current of carbon dioxide being passed during the whole operation and small quantities of dilute hydrochloric acid added from time to time. When the colour had been completely discharged, the whole was filtered hot; the nearly neutral filtrate concentrated considerably under diminished pressure, when it was noticed that the liquid became pale brown and strongly alkaline.

The mass was several times extracted on the machine with ether and subsequently with chloroform, the extracts dried and evaporated, when a syrupy mass remained, which partly crystallised. After contact with porous porcelain the dry mass was dissolved in ether, the solution concentrated considerably and allowed to remain for several days in the ice-chest, when glistening prisms separated which melted at 122—124°, but the amount was only 0·37 gram:

0·1441 gave 0·3459 CO_2 and 0·0901 H_2O. C = 65·4; H = 6·9.
0·2072 „ 11·6 c.c. N_2 at 12° and 747 mm. N = 6·5.
$C_{12}H_{15}O_3N$ requires C = 65·2; H = 6·8; N = 6·3 per cent.

This substance was prepared several years before Pyman (T., 1910, **97**, 270) described 6:7-dimethoxy-2-methyltetrahydro*iso*quinolone, and the fact that its weak basic nature and other properties so exactly agree with those of the latter, coupled with the fact that this substance has been obtained from cryptopine in other ways, leaves no doubt as to its identity. The alkaline aqueous solution, which had been extracted with ether and chloroform, was concentrated to a small bulk, acidified with hydrochloric acid, and extracted twenty times on the machine with ether. The ethereal extract was dried, evaporated, and the residue digested with acetic anhydride for an hour when, on cooling, *m*-hemipinic anhydride melting at 175° separated. (Found, C = 58·0; H = 4·0. $C_{10}H_8O_5$ requires C = 57·7; H = 3·8 per cent.) The anhydride was hydrolysed by boiling with methyl-alcoholic potassium hydroxide and the acid recrystallised from water, when it separated in the crystals characteristic of *m*-hemipinic acid and melted at 200—202°. (Found, C = 53·0; H = 4·6. $C_{10}H_{10}O_6$ requires C = 53·1; H = 4·4 per cent.) In order to prove that the acid was *m*-hemipinic acid, and not hemipinic acid, it was converted into the ethylimide, which separated from alcohol in pale yellow needles and melted at 228—230°. The melting point of the ethylimide of *m*-hemipinic acid is 230°, whereas that of the ethylimide of hemipinic acid is 94°.

The Action of Nitric Acid on Cryptopine.

The Dinitrocryptopines, $C_{21}H_{21}(NO_2)_2O_5N$.

It has already been mentioned in the Introduction (p. 838) that cryptopine reacts readily with nitric acid with the formation of two (*A* and *B*) dinitrocryptopines, and these substances may be readily prepared under the following conditions. Cryptopine (5 grams) is mixed with ordinary concentrated nitric acid (30 c.c.) when it readily dissolves to a brown solution, and if the temperature, which has a tendency to rise appreciably, is kept at 25° for a few minutes it will usually remain at about this point for a considerable time. The liquid soon begins to effervesce, becomes dark brown, and overnight a crystalline precipitate separates and the colour of the acid fades to a pale orange. The precipitate is collected on asbestos in a Gooch crucible, washed first with concentrated nitric acid, then with water, and the pale yellow nitrate, which is almost insoluble in water, dissolved in much hot dilute sulphuric acid and filtered. On adding ammonia to the filtrate, a heavy, caseous precipitate separates, which soon becomes crystalline and chalky, and this is collected, washed with water, and then with boiling alcohol:

0·1078 gave 0·2161 CO_2 and 0·0472 H_2O.* C = 54·7; H = 4·8.
0·2200 „ 17·3 c.c. N_2 at 16° and 752 mm. N = 9·1.
$C_{21}H_{21}O_9N_3$ requires C = 54·9; H = 4·6; N = 9·1 per cent.

Dinitrocryptopine A does not melt at 250°, and when heated in a test-tube it suddenly puffs, yielding a dense carbonaceous mass and black smoke, and moisture condenses. It is characterised by its insolubility in the usual organic solvents, and it is also insoluble in methyl-alcoholic potassium hydroxide in the cold, but on boiling it dissolves to a brown solution, which gives no precipitation on the addition of water.

The salts are also mostly sparingly soluble; the hydrochloride is obtained as a mass of microscopic prisms when the base is dissolved in much boiling dilute hydrochloric acid and the solution stirred with a glass rod; the sulphate also crystallises well, and both this salt and the hydrochloride are much more readily soluble than the nitrate. The solution of the base in acetic acid gives, on the addition of concentrated sulphuric acid, a deep orange coloration.

Dinitrocryptopine B, $C_{21}H_{21}(NO_2)_2O_5N$.—When the nitric acid mother liquors from the preparation of *A* are diluted with water

* Both modifications of dinitrocryptopine decompose almost explosively when heated in a boat in the combustion tube, and for analysis it was therefore necessary to mix them with much powdered copper oxide.

a copious, crystalline precipitate separates, and this was collected, washed thoroughly, ground up with dilute ammonia, which removes much coloured impurity, and again transferred to the filter and washed. After drying on porous porcelain in the steam-oven the mass was digested with much boiling acetone, which leaves a small undissolved residue, probably consisting of *A*; the filtrate from this was concentrated and allowed to remain for some days, when a crust of colourless prisms gradually separated. After recrystallising from the same solvent the substance was analysed:

0·1061 gave 0·2149 CO_2 and 0·0451 H_2O. C = 55·2; H = 4·7.

0·2320 „ 17·7 c.c. N_2 at 12° and 760 mm. N = 9·1.

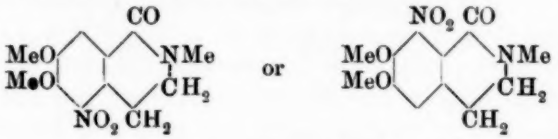
$C_{21}H_{21}O_9N_3$ requires C = 54·9; H = 4·6; N = 9·1 per cent.

Dinitrocryptopine B melts at about 213° to a dark mass, and is very sparingly soluble in acetone, but more readily so in boiling methyl ethyl ketone; it is also very sparingly soluble in boiling alcohol, but on cooling it separates in groups of microscopic prisms. Not only is it much more readily soluble in organic solvents than *A*, but its salts are also more readily soluble. The nitrate of base *A*, for example, is almost insoluble even in boiling water, but base *B* dissolves readily in warm dilute nitric acid; on cooling a semi-solid caseous salt separates which dissolves readily in hot water, but on rubbing it becomes crystalline, and in this condition is rather sparingly soluble. The sulphate dissolves readily in hot water, and is deposited on cooling as a gummy mass; the hydrochloride is also readily soluble in hot water, and the solution gives with mercuric chloride a milky precipitate which soon crystallises and is soluble in much boiling water. The platinichloride separates on the addition of platinic chloride to the cold solution of the hydrochloride as a pale yellow, caseous precipitate, which on warming becomes crystalline; the picrate is a canary-yellow, crystalline precipitate.

The Oxidation of Cryptopine by Dilute Nitric Acid.

When cryptopine is oxidised by dilute nitric acid it yields a great variety of products, the formation of which depends on the strength of the acid employed, the temperature, and time during which the mixture is heated. No useful purpose would be served by detailing the large number of experiments which have been made in this connexion, but the following experiment may be described in order to indicate the direction in which the decomposition proceeds. Cryptopine (5 grams) was mixed with dilute nitric acid (800 c.c. of D 1·2) and gradually heated in a flask on the steam-bath; the sparingly soluble nitrate which separated at first soon dissolved, and after heating for three hours the orange liquid deposited on keeping in the ice-chest an orange, crystalline crust on

the walls of the flask. The liquid was decanted, the precipitate dissolved in boiling water, and after concentrating to a low bulk and leaving, a small amount of a red precipitate separated, which was removed by filtration. The filtrate was further concentrated, cooled, and vigorously stirred mechanically, when an orange, crystalline precipitate separated in quantity. This substance was collected, dried in the steam-oven, and is evidently 5(or 8)-*nitro*-6:7-*dimethoxy*-2-*methyltetrahydro*isoquinolone:



0·1585 gave 0·3144 CO_2 and 0·0785 H_2O. C = 54·1; H = 5·5.
0·1469 „ 13·7 c.c. N_2 at 19° and 762 mm. N = 10·6.
$C_{12}H_{14}O_5N_2$ requires C = 54·1; H = 5·3; N = 10·5 per cent.

This substance darkens above 180°, becomes black at 210°, and melts and decomposes at 245—250°, yielding a black froth. It is very sparingly soluble in water, alcohol, or acetic acid, and possesses only very feeble basic properties. When it is digested with dilute potassium hydroxide, it dissolves to a yellow solution, and on precipitation with hydrochloric acid and recrystallisation from acetic acid an orange substance is obtained, which melts at about 245° and evidently consists of the original methyltetrahydro*iso*quinolone derivative.

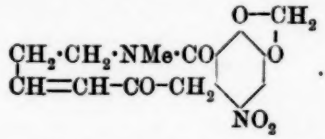
When the dilute nitric acid mother liquor from the above keto-derivative was concentrated under diminished pressure, it yielded a crop of yellow crystals which was collected and extracted with cold dilute ammonia (*F*). The almost colourless residue was thoroughly washed, dried, and fractionally crystallised from alcohol, when it yielded four substances, namely, *A* (m. p. above 260°), *B* (m. p. 213°), *C* (m. p. 214°), and *D* (m. p. 187°), and of these *C* and *D* were present in the larger quantity.

The substance *A* is very sparingly soluble, separates in minute needles, and consists of m-*hemipinimide*, $(MeO)_2C_6H_2<^{CO}_{CO}>NH$. (Found, C = 57·9; H = 4·6; N = 6·5. $C_{10}H_9O_4N$ requires C = 58·0; H = 4·3; N = 6·7 per cent.) Substance *B* crystallised from acetone in nearly colourless prisms, and is *dinitrocryptopine B*. (Found, C = 54·9; H = 4·7; N = 9·3. $C_{21}H_{21}O_9N_3$ requires C = 54·9; H = 4·6; N = 9·1 per cent.) The substance *C* is very sparingly soluble in boiling alcohol, and separates as a voluminous mass of pale yellow needles which melt at 214° with evolution of gas to a black froth. It gives no characteristic colour when

sulphuric acid is added to the solution of a trace in a drop of acetic acid:

0·1121 gave 0·2307 CO_2 and 0·0474 H_2O. C=56·2; H=4·7.
0·3887 „ 28·3 c.c. N_2 at 9° and 759 mm. N=8·8.
$C_{15}H_{14}O_6N_2$ requires C=56·6; H=4·4; N=8·8 per cent.

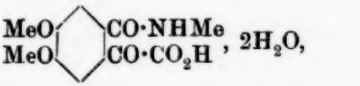
It is possible that this substance is produced by the removal of the 5:6-dimethoxybenzene ring, and may have the constitution:



but the available material was too small to allow of this supposition being tested by a methoxy-determination or otherwise.

The substance *D*, melting at 187°, is *nitrocryptopine*. (Found, C=60·8; H=5·3; N=6·9. $C_{21}H_{22}O_7N_2$ requires C=60·9; H=5·3; N=6·8 per cent.)

The brown ammoniacal filtrate (*F*), obtained as described above, was digested with animal charcoal, concentrated considerably, acidified, and allowed to remain, when it gradually deposited a thin crust of *cryptopidic acid* (see p. 895), and the filtrate from this acid, after further concentration, yielded stellate groups which were readily soluble in hot water and crystallised in colourless plates. This substance melted at about 104—107° to a yellow syrup, and was found on careful examination to be 3:4-*dimethoxy*-6-*methylcarbamylphenylglyoxylic acid*:



which Mason and Perkin (T., 1914, **105**, 2018) had previously obtained by the oxidation of papaveraldine methosulphate with alkaline permanganate.

The identity was proved by analysis (Found, C=47·8; H=5·7; N=4·5. $C_{12}H_{13}O_6N,2H_2O$ requires C=47·5; H=5·6; N=4·6 per cent.) and by the fact that when boiled with dilute nitric acid, or when hydrogen peroxide was added to its solution in hot dilute hydrochloric acid, it was quantitatively converted into methyl-*m*-*hemipinimide*, $(MeO)_2C_6H_2<^{CO}_{CO}>NMe$, which melted at 260—262°.

It is curious that the glyoxylic acid should have resisted the action of the dilute nitric acid, but this is probably due to the acid employed being very weak and the temperature of concentration (under about 30 mm.) being very low.

Cryptopidic Acid, $C_{18}H_{21}O_7N$. (Formula, p. 837.)

Cryptopine is not oxidised to cryptopidic acid with the same readiness as berberine yields berberidic acid (Dobbie and Lauder, T., 1902, **81**, 157), but it is usually produced, although always in very small quantity, when cryptopine is oxidised with very dilute nitric acid (compare p. 893), and the best conditions appear to be the following:

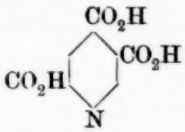
Cryptopine (25 grams) is mixed with concentrated nitric acid (45 c.c.) and water (1500 c.c.) when it dissolves, and in a short time the nitrate separates. The whole is placed on a vigorously boiling water-bath for six hours, nearly neutralised by the addition of about 10 grams of anhydrous sodium carbonate, concentrated to about a quarter of its bulk, and left in bottles in the ice-chest for at least two months, during which a thin crust gradually forms on the walls of the bottles. This crust, which consists essentially of a mixture of nitrocryptopine and cryptopidic acid, is collected and warmed with dilute sodium carbonate, when the acid dissolves, leaving the nitrocryptopine as a heavy, pale ochreous precipitate. This is collected, dissolved in much boiling alcohol, and the solution concentrated, when on keeping it deposits brilliant, well-developed, slightly brown prisms which melt at 187—189° and give on analysis C = 60·6; H = 5·5; N = 6·8, whereas $C_{21}H_{22}(NO_2)O_5N$ requires C = 60·9; H = 5·3; N = 6·8 per cent. Nitrocryptopine had already been prepared by Hesse (*loc. cit.*, p. 299) from cryptopine by the action of very dilute nitric acid (D 1·06) at 50—60°, and is described as crystallising in prisms and melting at 185°. Several of the salts have also been described by Hesse, and of these the nitrate, which is almost insoluble in dilute nitric acid and crystallises in small prisms, is perhaps the most characteristic. The alkaline filtrate from the nitrocryptopine was rendered just acid to Congo paper by the addition of dilute hydrochloric acid and the filtered solution left for two days in the ice-chest, during which a hard, crystalline crust separated, and a further considerable crop was obtained from the mother liquor by allowing it slowly to concentrate over sulphuric acid.

This crystalline mass, which consisted of almost pure cryptopidic acid and melted at about 180—182° to a black mass, was recrystallised from boiling water, in which it is rather sparingly soluble and from which it separates in amber prisms. Two different preparations gave on analysis:

I. 0·1006 gave 0·2179 CO_2 and 0·0533 H_2O. C = 59·1; H = 5·9.
II. 0·1050 „ 0·2292 CO_2 „ 0·0555 H_2O. C = 59·5; H = 5·9.
II. 0·3795 „ 12·3 c.c. N_2 at 15° and 767 mm. N = 3·8.

$C_{18}H_{21}O_7N$ requires C = 59·5; H = 5·8; N = 3·8 per cent.

Cryptopidic acid darkens at 175°, and decomposes to a black mass at about 185—187°. It is sparingly soluble in methyl alcohol, ethyl acetate, benzene, or chloroform even on boiling, but dissolves rather readily in boiling acetic acid, yielding the acetate (see p. 896); long boiling with acetic acid is, however, to be avoided, as this decomposes the acid and the solution becomes black. The solution of the acid in dilute sodium carbonate does not decolorise permanganate readily in the cold, but does so on warming, and, although this oxidation was investigated with a considerable quantity of the acid (2 grams), with the exception of a large amount of oxalic acid and some *m*-hemipinic acid, nothing definite could be isolated. In this respect cryptopidic acid differs widely from berberidic acid and corydic acid, which yield pyridinetricarboxylic and methylpyridinetricarboxylic acids:



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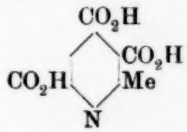


respectively on oxidation (Dobbie and Lauder, T., 1902, **81**, 145, 157). When a trace of cryptopidic acid dissolved in a drop of acetic acid is mixed with sulphuric acid, a pale carmine solution is produced which in a minute or two becomes very intense, and on the addition of water the colour changes first to orange and then to yellow.

Methoxy-determination: 0·0566 gave 0·0724 AgI. MeO = 16·9.
$C_{18}H_{21}O_7N$, containing 2MeO, requires MeO = 17·1 per cent.

Titration.—Like berberidic acid, cryptopidic acid, $C_{18}H_{21}O_7N$, behaves on titration as a monobasic acid, but is in reality dibasic, since it yields a silver salt of the formula $C_{18}H_{19}Ag_2O_7N$. The titration was carried out by dissolving the acid in excess of *N*/10-sodium hydroxide and titrating back with *N*/10-sulphuric acid, when it was found that 0·3089 neutralised 8·7 c.c. NaOH, whereas this amount of a monobasic acid, $C_{18}H_{21}O_7N$, should neutralise 8·5 c.c. A second titration gave an almost identical result.

On adding excess of sulphuric acid to the products of these titrations and leaving in the ice-chest the acid very gradually separated in magnificent, glistening, amber prisms.

The Silver Salt.—The hot concentrated aqueous solution of the acid gives no precipitate on the addition of silver nitrate, but when silver nitrate is added to the slightly alkaline solution of the ammonium salt, a white, amorphous precipitate separates. This dissolves on boiling, and the filtered solution deposits a heavy, chalky precipitate, which was collected, washed, and dried over phosphoric

oxide since the salt melts to a pale resin in the steam-oven. When this salt is heated it explodes, and the silver had therefore to be determined as chloride:

0·1076 gave 0·1461 CO_2 and 0·0346 H_2O. C = 37·1; H = 3·5.
0·2114 „ 0·1051 AgCl. Cl = 37·4.
$C_{18}H_{19}Ag_2O_7N$ requires C = 37·4; H = 3·3; Ag = 37·4 per cent.

The *hydrochloride*, $C_{13}H_{21}O_7N,HCl$, was obtained by dissolving the acid in warm concentrated hydrochloric acid, when on keeping a lemon-yellow, crystalline mass separated which, after drying on porous porcelain, gave the following analytical results:

0·1211 gave 0·2356 CO_2 and 0·0624 H_2O. C = 53·1; H = 5·7.
0·2112 „ 0·0711 AgCl. Cl = 8·3.
$C_{18}H_{21}O_7N,HCl$ requires C = 54·0; H = 5·5; Cl = 8·9 per cent.

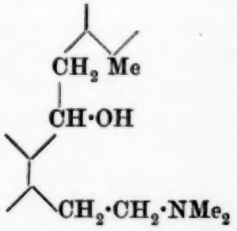
This *hydrochloride* darkens at 180°, is black at 190°, and decomposes with evolution of gas at about 202°. It is dissociated by boiling with water, and on cooling cryptopidic acid separates in yellow prisms.

The Acetate.—Cryptopidic acid is sparingly soluble in glacial acetic acid in the cold, but it dissolves on warming, and if the test-tube containing the solution is placed in boiling water the acetate soon begins to separate in heavy crystals. After a few minutes the substance was collected, washed with acetic acid, in which it is very sparingly soluble, dried on porous porcelain, and analysed:

0·1107 gave 0·2312 CO_2 and 0·0579 H_2O. C = 56·9; H = 5·8.
$C_{20}H_{25}O_9N$ requires C = 56·7; H = 5·9 per cent.

This *acetate* darkens rapidly above 175°, is black at 190°, and decomposes with evolution of gas at about 197—200°; it is characterised by being almost insoluble even in boiling acetic acid. It dissolves readily in sodium carbonate to an almost colourless solution, and on acidifying cryptopidic acid gradually separates. The acetate dissolves in concentrated sulphuric acid to an intense carmine solution, which on the addition of water becomes orange and finally lemon-yellow.

Tetrahydromethylcryptopine,



This substance is readily prepared by dissolving cryptopine methosulphate (20 grams, p. 880) in hot 5 per cent. sulphuric acid

(1 litre) in a porcelain basin and rapidly adding a large excess of 4 per cent. sodium amalgam (500 grams), the whole being vigorously stirred and kept strongly acid by the addition from time to time of small quantities of 25 per cent. sulphuric acid. The product is allowed to cool, filtered, and mixed with a considerable excess of 30 per cent. sodium hydroxide, when a syrupy mass separates which is extracted with ether. After washing and drying over potassium carbonate the ethereal solution is concentrated to a small bulk and allowed to remain in the ice-chest, when a crust of magnificent, glistening prisms gradually forms. For analysis, the substance was recrystallised from ether and dried at 90°:

0·1042 gave 0·2594 CO_2 and 0·0705 H_2O. C = 67·9; H = 7·5.
0·1178 „ 0·2933 CO_2 „ 0·0827 H_2O. C = 68·1; H = 7·7.
0·2675 „ 8·7 c.c. N_2 at 14° and 736 mm. N = 3·7.
$C_{22}H_{29}O_5N$ requires C = 68·2; H = 7·5; N = 3·6 per cent.

Methoxy-determination: 0·1964 gave 0·2424 AgI. MeO = 16·3, whereas $C_{22}H_{29}O_5N$, containing 2MeO, requires MeO = 16·0 per cent.

Tetrahydromethylcryptopine melts at 106—107° and is readily soluble in methyl alcohol, acetone, ethyl acetate, or benzene, but sparingly so in light petroleum. It may be recrystallised from a mixture of benzene and light petroleum, but ether is the better solvent for this purpose. When a small quantity is rapidly heated in a test-tube it distils almost without residue, there is a distinct odour of dimethylamine, and the almost colourless, resinous distillate is only partly soluble in dilute sulphuric acid and has the odour of veratrole. The solution of a trace of tetrahydromethylcryptopine in a drop of acetic acid gives a deep port-wine coloration on the addition of concentrated sulphuric acid. The base dissolves readily in concentrated hydrochloric acid or 50 per cent. sulphuric acid, and when these solutions are boiled they become first yellow, then brownish-violet, and finally nearly black. The salts are mostly readily soluble in water, the *hydrochloride* separates from a concentrated solution in colourless, prismatic needles, and the *nitrate* is obtained by rubbing the base with excess of dilute nitric acid as a crystalline mass which dissolves readily in warm water, but if the solution in dilute nitric acid is warmed it becomes momentarily pink, then brown, and an oil separates which has the odour of methylpiperonal (p. 907). When potassium iodide is added to the solution of the hydrochloride a milkiness is produced and a colourless gum separates which crystallises with difficulty. This dissolves in hot water, and if the solution is cooled and rubbed a crystalline *hydriodide* separates which is very sparingly soluble in water. The addition of mercuric chloride to the solution of the hydrochloride

gives a caseous precipitate which is appreciably soluble in hot water and gradually crystallises. The *platinichloride*,

$$(C_{22}H_{29}O_5N)_2H_2PtCl_6,$$

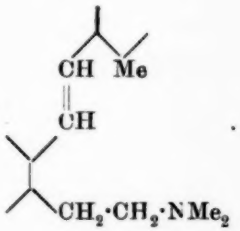
is obtained as a pale yellow precipitate when platinic chloride is added to the rather dilute solution of the hydrochloride. When warmed with water it becomes viscid and melts to a yellow resin, which again solidifies on cooling:

0·2919 gave 0·0483 Pt. Pt = 16·5.

$(C_{22}H_{29}O_5N)_2H_2PtCl_6$ requires Pt = 16·5 per cent.

The addition of auric chloride to the warm solution of the hydrochloride gives an uninviting, viscid, drab mass which rapidly darkens and becomes almost black; picric acid gives a yellow, amorphous precipitate which melts to an orange oil under hot water.

Anhydrotetrahydromethylcryptopine,



The hydrochloride of this substance was first obtained from tetrahydromethylcryptopine by the action of phosphoryl chloride. The substance (1 gram) was boiled with freshly distilled phosphoryl chloride (3 grams) and after the action had subsided the excess was distilled off under diminished pressure and the crystalline residue dissolved in the least quantity of boiling water, when, on cooling, the hydrochloride of anhydrotetrahydromethylcryptopine separated in characteristic, microscopic needles. Subsequently it was found that a cleaner product is obtained by substituting acetyl chloride for phosphoryl chloride, and the conditions of preparation finally adopted were the following: Tetrahydromethylcryptopine (5 grams) is heated in a reflux apparatus with acetyl chloride (15 c.c.) just to boiling, when the white precipitate first produced gradually but completely dissolves, and after fifteen minutes the excess of acetyl chloride is distilled off, during which a white, crystalline substance commences to separate and the residue is a colourless, fluorescent, crystalline cake. This dissolves sparingly in boiling water and the hydrochloride separates, on slowly cooling, as a crystalline cake which under the microscope is seen to consist of a long, slender prisms with bevelled edges. In order to obtain the free base the solution of the hydrochloride in boiling water is mixed with excess of potassium hydroxide, when a syrup separates which on cooling only gradu-

ally crystallises, but falls at once to a crystalline powder when it is rubbed with methyl alcohol. The precipitate is collected and recrystallised from methyl alcohol, with which it readily forms supersaturated solutions and from which it separates in splendid prisms with a faint yellow tinge and beautiful bluish-violet fluorescence. These crystals contain methyl alcohol of crystallisation, and when dried in the water-oven become chalky and lose their fluorescence:

1·0113 lost, on drying at 90°, 0·0738. MeOH = 7·3.

$C_{22}H_{27}O_4N$,MeOH requires MeOH = 7·9 per cent.

0·1108 gave 0·2894 CO_2 and 0·0754 H_2O. C = 71·2; H = 7·5.

0·1138 „ 0·2974 CO_2 „ 0·0754 H_2O. C = 71·3; H = 7·3.

0·4543 „ 16·4 c.c. N_2 at 13·8° and 760 mm. N = 4·2.

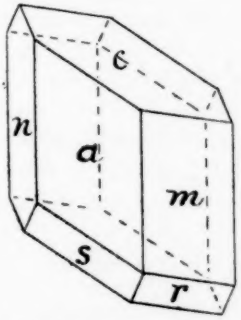
$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3; N = 3·8 per cent.

Anhydrotetrahydromethylcryptopine melts at 106—107° and dissolves readily in boiling methyl alcohol, but sparingly so in the cold; it is readily soluble in acetone, ethyl acetate, or benzene, but sparingly so in cold light petroleum. When a trace of the substance dissolved in a drop of acetic acid is mixed with sulphuric acid, a reddish-violet solution is produced which soon becomes intense claret, and if the test-tube is placed in boiling water the colour of the solution becomes almost like that of permanganate. The solution in acetic acid also becomes claret coloured on the addition of nitric acid.

The measurement of the crystals obtained from methyl alcohol was made by Mr. A. Scott, who finds that the system is triclinic, with the axial ratios: $a:b:c = 1·290:1:1·705$; $\alpha = 120°14'$, $\beta = 95°38'$, $\gamma = 92°58'$.

The forms observed were: $a\{100\}$, $c\{001\}$, $m\{110\}$, $n\{11\bar{0}\}$, $r\{\bar{1}01\}$, $o\{11\bar{2}\}$. The habit was stout prismatic, as shown in Fig. 2. Following are the measured and calculated angles:

FIG. 2.



Anhydrotetrahydromethylcryptopine.

Table of Measured and Calculated Angles.

Angle.	No.	Limits.	Mean.	Calc.
$am = 100 : 110$	6	57°0′ — 57°7′	57°3′	57°7′
$an = 100 : 1\bar{1}0$	8	56 45 — 56 53	*56 50	—
$mn = 110 : 1\bar{1}0$	7	66 0 — 66 7	*66 3	—
$ar = \bar{1}00 : \bar{1}01$	3	43 25 — 43 34	*43 34	—
$cr = 001 : \bar{1}01$	2	51 22 — 51 35	51 28	51 23
$ca = 001 : 100$	3	84 59 — 85 6	*85 3	—
$cm = 001 : 110$	4	62 6 — 62 13	*62 9	—
$co = 001 : \bar{1}\bar{1}2$	3	60 35 — 60 47	60 41	60 37
$rn = \bar{1}01 : \bar{1}10$	2	46 35 — 46 38	46 36	46 34
$ro = \bar{1}01 : \bar{1}\bar{1}2$	2	45 56 — 45 59	45 57	46 0

Salts of Anhydrotetrahydromethylcryptopine.

The salts of tetrahydromethylcryptopine (p. 897) are readily soluble in water and crystallise with difficulty, but, on the other hand, anhydrotetrahydromethylcryptopine is characterised by the fact that its salts are very sparingly soluble in water, and especially in dilute acids, and by the ease with which they crystallise. The *hydrochloride* is obtained, as already described (p. 898), by the action of acetyl chloride on tetrahydromethylcryptopine, and is also readily prepared by mixing the anhydro-base with dilute hydrochloric acid. It separates when its solution in boiling water is allowed to cool slowly in prismatic needles which have a beautiful lilac fluorescence in the dry state, but not in solution. It is very sparingly soluble in cold dilute hydrochloric acid:

0·2976 gave 0·1054 AgCl. Cl = 8·7.

$C_{22}H_{27}O_4N,HCl$ requires Cl = 8·7 per cent.

The *sulphate* separates from water, in which it is sparingly soluble, as a felted mass of needles which fluoresce in the dry state, but not in solution, and the *nitrate* is almost insoluble in cold dilute nitric acid. The solution of the hydrochloride gives with picric acid a bright yellow, amorphous powder which on boiling becomes crystalline, and mercuric chloride produces a milky solution which on warming clears, and a crystalline salt separates on cooling and rubbing.

The *platinichloride* is obtained on the addition of platinic chloride to the warm solution of the hydrochloride as a drab, caseous precipitate, which on boiling with water becomes chalky:

0·2216 gave 0·0377 Pt. Pt = 17·0.

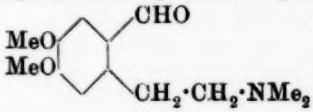
$(C_{22}H_{27}O_4N)_2H_2PtCl_6$ requires Pt = 17·0 per cent.

Oxidation of Anhydrotetrahydromethylcryptopine.

This oxidation may be carried out by means of aqueous permanganate in the usual manner, but proceeds more smoothly in acetone

solution. The pure anhydro-base (5 grams) dissolved in acetone (150 c.c.) in a flask fitted with a mechanical stirrer, is cooled to 5° and then finely powdered permanganate, which has been passed through a sieve of 80 meshes to the inch (5 grams), is added in small quantities at a time, the whole being vigorously shaken and stirred until each addition has been decolorised. The temperature, which has a tendency to rise, must not exceed 5° during the whole operation. After remaining overnight the product is collected, the precipitate (*A*) washed with acetone, and the acetone distilled from the filtrate under somewhat diminished pressure, when a viscid, brown syrup containing 4 : 5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde and 5 : 6-methylenedioxy-*o*-tolualdehyde remains (*B*, see below). The precipitate (*A*) is repeatedly extracted with hot water, the solution concentrated and acidified when a chalky precipitate of 5 : 6-methylenedioxy-*o*-toluic acid containing some 4 : 5-dimethoxyhomophthalic acid (*C*, p. 916) separates, which is collected, washed, and dried on porous porcelain. The aqueous filtrate from these acids is extracted at least ten times on the machine with large quantities of ether, the extracts dried and evaporated to a small bulk, and left in the ice-chest, when pale ochreous crusts of crude *N*-formyl-4 : 5-dimethoxy-2-β-methylaminoethylbenzoic acid separate, together with some 5 : 6-methylenedioxy-*o*-toluic acid and *m*-hemipinic acid (*D*, p. 923).

4 : 5-*Dimethoxy*-2-β-*dimethylaminoethylbenzaldehyde*,



The syrupy acetone extract of the product of the above oxidation (*B*), which at times partly crystallises owing to the separation of 5 : 6-methylenedioxy-*o*-tolualdehyde, is dissolved in ether and extracted with several small quantities of dilute hydrochloric acid (1 vol. of concentrated hydrochloric acid to 3 vols. of water), the ethereal solution is washed with water, dried, and evaporated, and leaves a syrupy residue of crude 5 : 6-methylenedioxy-*o*-tolualdehyde (*E*, p. 907), which crystallises on keeping. The hydrochloric acid extract is mixed with a large excess of 50 per cent. sodium hydroxide and repeatedly extracted with ether (*F*),* the ethereal solution

* When the strongly alkaline aqueous liquors (*F*) from several such operations were left for several weeks in a dark place, a small quantity of an orange, crystalline precipitate was deposited which was collected on an asbestos filter, drained on porous porcelain and dissolved in boiling methyl alcohol. After filtering and adding twice the volume of water, the clear solution deposited a crust of deep orange, glistening needles which became

dried over potassium carbonate and evaporated, when a viscid, brown syrup remains.

This is *rapidly* * distilled under diminished pressure (10 mm.), all that passes over below 220° being collected, and the considerable dark brown residue which on cooling sets to a mass like shellac is neglected. The distillate is then *rapidly* refractionated, when most distils at 190—192°/10 mm. as a colourless syrup with a characteristic basic odour:

0·1861 gave 0·4467 CO_2 and 0·1269 H_2O. C = 65·5; H = 7·6.
0·2102 „ 0·5072 CO_2 „ 0·1456 H_2O. C = 65·7; H = 7·7.
0·3428 „ 18 c.c. N_2 at 12° and 754 mm. N = 6·1.
$C_{13}H_{19}O_3N$ requires C = 65·8; H = 8·0; N = 5·9 per cent.

4 : 5-*Dimethoxy*-2-*β*-*dimethylaminoethylbenzaldehyde* is readily soluble in water, yielding a strongly alkaline solution which fumes in contact with hydrogen chloride; the addition of platinic chloride to the dilute solution of the hydrochloride gives no precipitate, and

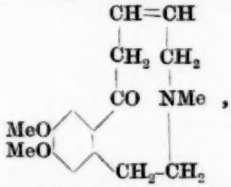
lemon-yellow in the water-oven. This substance was recrystallised and gave the following results on analysis:

0·1034 gave 0·2655 CO_2 and 0·0748 H_2O. C = 70·0; H = 8·0.
0·1132 „ 5·2 c.c. N_2 at 12·8° and 745 mm. N = 5·3.
$C_{16}H_{21}O_3N$ requires C = 69·8; H = 7·6; N = 5·1 per cent.

This substance softens at 90°, melts at 95°, and is characterised by the fact that a minute fragment on a watch glass yields on the addition of concentrated sulphuric acid, a most intense bluish-violet solution. The substance is also coloured deep sage green by nitric acid and, on warming, a yellowish-brown solution is produced which soon becomes yellow. It is sparingly soluble in water but readily so in dilute hydrochloric acid, yielding an orange solution, and, on the addition of platinic chloride, a deep yellow, amorphous precipitate of the platinichloride is produced. This curious salt becomes bright green when it is dried in the water-oven, and on keeping the green gradually gives place to yellow again.

0·1659 gave 0·0344 Pt. Pt = 20·7.
$(C_{16}H_{21}O_3N)_2H_2PtCl_6$ requires Pt = 20·3 per cent.

It is suggested that this base probably has the constitution



and is derived from cryptopidic acid (p. 837) by the elimination of two molecules of carbon dioxide, but the amount of substance available was so small that there was no possibility of testing this supposition experimentally.

* It is essential that the distillations of this base are carried out as rapidly as possible, otherwise considerable decomposition takes place, with the formation of resinous substances of high boiling point.

on boiling platinum is deposited; the solution of the base also reduces ammoniacal silver hydroxide with formation of a mirror.

Methylation.—When the solution of the above base in two volumes of acetone is mixed with excess of methyl iodide there is considerable rise of temperature, and a syrup separates which on rubbing rapidly crystallises.* The mass was collected, washed with alcohol, in which it is very sparingly soluble, dissolved in much boiling alcohol, and the solution concentrated by distillation under diminished pressure, when on keeping a glistening mass of crystals of 4:5-*dimethoxy*-2-*β*-*dimethylaminoethylbenzaldehyde methiodide* separated which melted at 200—202° and after recrystallisation at 202—203°:

0·1180 gave 0·1944 CO_2 and 0·0639 H_2O. C = 44·9; H = 6·0.
0·1781 „ 0·1083 AgI. I = 32·8.
$C_{14}H_{22}O_3NI$ requires C = 44·4; H = 5·8; I = 33·5 per cent.

The Oxime.—In order to prepare this characteristic derivative the methiodide (1 gram), dissolved in as little hot water as possible, is mixed with a hot concentrated solution of hydroxylamine hydrochloride. There is no immediate crystallisation, but on keeping glistening, heavy, pale amber prisms separate, and these were collected, washed with water, drained on porous porcelain, and dried in the water-oven:

0·1959 gave 12·3 c.c. N_2 at 17° and 770 mm. N = 7·4.
$C_{14}H_{23}O_3N_2I$ requires N = 7·1 per cent.

The glistening prisms of this oxime become opaque on drying at 95°, melt at about 223°, and then decompose with evolution of gas and formation of a dark brown syrup.

4:5-*Dimethoxy*-2-*vinylbenzaldehyde*, $(MeO)_2C_6H_2(CHO)\cdot CH{:}CH_2$.

This substance is obtained, together with trimethylamine, when 4:5-dimethoxy-2-*β*-dimethylaminoethylbenzaldehyde methiodide is boiled with potassium hydroxide. The methiodide (5 grams), dissolved in the least quantity of boiling water, was mixed with potassium hydroxide (4 grams) in water (15 c.c.) and heated to boiling in a flask connected with a funnel dipping under dilute hydrochloric acid in a beaker. In a short time the solution clouded and a viscid, yellow syrup of crude dimethoxyvinylbenzaldehyde separated,

* When the base was treated in acetone solution with methyl iodide in the presence of a trace of alkali, the yellow condensation product melting at 255°, and described on p. 906, was obtained. In later experiments, the methylation was carried out in ethereal solution, and the yellow mass which separated recrystallised from alcohol.

which on cooling became semi-solid and was collected and washed carefully. The acid solution in the beaker was evaporated to dryness and the residue, which was completely soluble in alcohol, dissolved in a little water, mixed with excess of platinic chloride, and allowed to remain for several days in the ice-chest, when stout, orange prisms of trimethylamine platinichloride separated. (Found, Pt = 35·4. $2NMe_3,H_2PtCl_6$ requires Pt = 35·1 per cent.)

The crude dimethoxyvinylbenzaldehyde could not be recrystallised, and much difficulty was experienced in purifying it, but this was ultimately accomplished in the following way. The crude, viscid, yellow mass was dissolved in methyl alcohol and mixed with a considerable excess of semicarbazide acetate, when almost immediately a crystalline substance began to separate and soon the whole became a paste. The precipitate was collected, and washed with methyl alcohol until all the yellow impurity had been removed and a colourless, crystalline powder remained. This *semicarbazone* of 4 : 5-*dimethoxy*-2-*vinylbenzaldehyde* was then recrystallised from boiling methyl alcohol, in which it is very sparingly soluble and from which it separates as a satiny mass like benzoic acid. It darkens at 220° and melts at about 226° with evolution of gas to a dark red liquid:

0·1303 gave 17·4 c.c. N_2 at 10° and 769 mm. N = 16·2.

$C_{12}H_{15}O_3N_3$ requires N = 16·9 per cent.

Attempts to hydrolyse this semicarbazone and thus to obtain the corresponding aldehyde were for a long time unsuccessful owing to the susceptibility of the aldehyde to the action of acids. Thus the semicarbazone is coloured pink by hydrochloric acid, the solution clouds and deposits an amorphous precipitate, and on warming the whole becomes an intense permanganate colour, and a similar change takes place even when the semicarbazone is boiled with oxalic acid and to a less extent with succinic acid. Ultimately, after experimenting with a great variety of acids and other substances, it was found that decomposition by pyruvic acid led to the desired result. The semicarbazone (1 gram) is warmed with water (2 c.c.) and pyruvic acid (1·5 c.c.) on the water-bath until a clear, brown solution is just produced, longer heating being carefully avoided, otherwise decomposition occurs with the formation of a resinous mass. The product is left for ten minutes, mixed with water (10 c.c.), neutralised with potassium carbonate, and the oil extracted with ether, when most of the colouring matter remains in the aqueous layer. On evaporating the lemon-yellow ethereal solution, a viscid, yellow syrup is obtained which, when rubbed, soon begins to crystallise in starry groups. After leaving in contact with porous porcelain, which removes much impurity, the residue is

dissolved in boiling light petroleum (b. p. 50—60°), filtered, allowed to cool, decanted from the oil which separates, and left to concentrate by exposure to the air, and after repeating this process several times colourless, leafy masses are obtained, but the purification is most troublesome:

0·1238 gave 0·3119 CO_2 and 0·0686 H_2O. C = 68·7; H = 6·2.

$C_{11}H_{12}O_3$ requires C = 68·8; H = 6·2 per cent.

4:5-*Dimethoxy-2-vinylbenzaldehyde* melts at 54—55° and is readily soluble in the ordinary organic solvents, but sparingly so in cold light petroleum. It dissolves in concentrated hydrochloric acid, the liquid rapidly becomes pink and cloudy, and on warming an intense pink solution is produced, and a substance separates which has a green metallic lustre and resembles rosaniline. A crystal splinter on a watch-glass is coloured deep greenish-brown by concentrated sulphuric acid, and then dissolves with a fine deep green colour with violet streaks at the edge. On exposure to the air the whole becomes intense indigo-blue, the addition of water does not destroy the colour, and an indigo powder separates.

The Oxime.—This characteristic derivative was prepared by adding a concentrated aqueous solution of hydroxylamine hydrochloride (1 gram) and sodium acetate (1 gram) to the solution of dimethoxyvinylbenzaldehyde (1 gram) in methyl alcohol (10 c.c.). In a short time stout prisms commenced to separate, and after remaining overnight water was added, the precipitate collected, and recrystallised from 70 per cent. methyl alcohol:

0·2926 gave 16·4 c.c. N_2 at 18° and 760 mm. N = 6·5.

$C_{11}H_{13}O_3N$ requires N = 6·7 per cent.

The *oxime* of 4:5-*dimethoxy-2-vinylbenzaldehyde* melts at 126° and is very readily soluble in methyl alcohol; from dilute methyl alcohol it separates on slowly cooling in well-developed, colourless, glistening prisms.

Methylation of 4:5-*Dimethoxy-2-β-methylaminoethylbenzaldehyde.*

This base, prepared by the method described by Pyman (T., 1909, **95**, 1272), suspended in ether, was mixed with an excess of methyl iodide in a reflux apparatus and gently heated on the water-bath, when a heavy, yellow, crystalline cake gradually separated.* This product, which contained the hydriodide of the original substance,

* In one experiment, the crude base, containing doubtless traces of sodium hydroxide, was methylated in acetone solution, when, after boiling for a short time on the water-bath, crystallisation commenced and a large crop of a pale yellow, crystalline mass separated.

There can be no doubt that this substance, which is very sparingly soluble

$X{\cdot}CH_2{\cdot}CH_2{\cdot}NHMe,HI$ (i), the hydriodide of the dimethyl base, $X{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,HI$ (ii), and the quaternary salt,

$$X{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I \text{ (iii)},$$

was fractionally crystallised from water and subsequently from 97 per cent. alcohol, when (iii) was obtained in small quantity as a pale yellow, crystalline mass which softened at 198° and melted at 203°. (Found, I = 32·9. $C_{14}H_{22}O_3NI$ requires I = 33·5 per cent.) Since this substance yielded trimethylamine and 4:5-dimethoxy-2-vinylbenzaldehyde on boiling with potassium hydroxide and is converted by hydroxylamine into the characteristic oxime, $C_{14}H_{23}O_3N_2I$ (m. p. 223°; compare p. 903), there can be no doubt that it is identical with the 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde methiodide obtained as described on p. 903.

During the fractional crystallisation of the crude product of the action of methyl iodide on dimethoxymethylaminoethylbenzaldehyde a salt was isolated which was more readily soluble than the substance melting at 203° and separated from alcohol as a voluminous mass of colourless needles. Analysis showed that this salt consisted of the almost pure hydriodide of 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde, $(MeO)_2C_6H_2(CHO){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,HI$ (ii):

0·2330 gave 0·1506 AgI. I = 34·9.
0·3514 „ 11·2 c.c. N_2 at 10° and 756 mm. N = 3·8.
$C_{13}H_{19}O_3N,HI$ requires I = 34·8; N = 3·8 per cent.

This salt melted at about 190°, but was not quite pure, since the concentrated aqueous solution when gently warmed with 50 per cent. sodium hydroxide yielded a syrup which contained a small quantity of the methiodide melting at 203°. The alkaline liquid was repeatedly extracted with ether, the ethereal solution dried over potassium carbonate, evaporated, and the residue rapidly distilled, when a syrup passed over at 190—193°/10 mm., which on analysis gave C = 65·4; H = 7·9; N = 6·0, whereas $C_{13}H_{19}O_3N$ requires C = 65·8; H = 8·0; N = 5·9 per cent. That this substance is identical with 4:5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde (p. 902) was proved by conversion into the methiodide melting at 203°.

in boiling alcohol and separates in glistening, iridescent, yellow plates (m. p. 255°), has the constitution

$$(MeO)_2C_6H_2\begin{cases}CH{:}CH{\cdot}CO{\cdot}CH_3\\ CH_2{\cdot}CH_2{\cdot}NMe_3I\end{cases}$$

(compare Pyman, T., 1909, **95**, 1268).

0·1013 gave 0·1825 CO_2 and 0·0570 H_2O. C = 49·1; H = 6·2.
0·2694 „ 6·9 c.c. N_2 at 13° and 746 mm. N = 3·0.
0·2537 „ 0·1426 AgI. I = 30·4.
$C_{17}H_{26}O_3NI$ requires C = 48·7; H = 6·2; N = 3·3; I = 30·3 per cent.

Section III.

5 : 6-*Methylenedioxy*-o-*tolualdehyde* (*Methylpiperonal*), $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$.

The formation of this interesting aldehyde by the oxidation of anhydrotetrahydromethylcryptopine and its separation from 4 : 5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde is described on p. 901 (*E*).

The crude aldehyde is readily purified by distillation in a current of steam, and is thus obtained as a rather waxy, colourless, crystalline mass which separates from light petroleum (b. p. 60—80°) in massive groups of striated and jagged plates like fern fronds. It crystallises from 70 per cent. methyl alcohol, in which it is readily soluble, in thin, glistening laminæ:

0·1147 gave 0·2777 CO_2 and 0·0510 H_2O. C = 66·0; H = 4·9.
$C_9H_8O_3$ requires C = 65·8; H = 4·9 per cent.

5 : 6-*Methylenedioxy*-o-*tolualdehyde* melts at 74—75°, distils at 154—155°/14 mm.,* and, especially when warmed, has a pronounced odour of piperonal. It dissolves in concentrated sulphuric acid to a deep yellow solution, which on keeping acquires a faint green tinge; on the addition of a little water the colour changes to intense brownish-violet.

FIG. 3.

Methylpiperonal.

Mr. T. V. Barker finds the crystals to be monoclinic with the axial ratios $a : b : c = 0{\cdot}4620 : 1 : 0{\cdot}4683$; $\beta = 113°16'$. The forms observed were: $b\{010\}$, $m\{110\}$, $c\{001\}$, $r\{\bar{1}01\}$, and, extremely

* The boiling point of piperonal in the same apparatus and under the same conditions was 144—145°.

rarely, $o\{\bar{1}11\}$. The habit is prismatic parallel to the vertical axis, and tabular parallel to $b\{010\}$, as is shown in Fig. 3. The results obtained by measurement and calculation of four crystals are given in the following table:

Table of Measured and Calculated Angles.

	ϕ.			ρ.		
Face.	Limits.	Mean.	Calc.	Limits.	Mean.	Calc.
m (110)	66°47′— 67°12′	*67°0′	—	—	90°0′	90°0′
c (001)	89 38 — 90 12	89 57	90°0′	23°10′—23°20′	*23 16	—
r ($\bar{1}01$)	269 36 —270 42	270 8′	270 0	33 54 —34 0	*33 57	—
o ($\bar{1}11$)	304 23 —304 43	304 33′	304 49	38 20 —38 26	38 23	39 21

Optics: extinction on $b(010)$ is 17° with the edge bm, and 5° with the edge bc. Twin crystals are very frequent with (100) as twin- and composition-plane.

Fedorov complex-symbol: $\begin{matrix} 6\,;7 \\ 67\frac{1}{2} \\ +2\frac{1}{2} \end{matrix}$ Determinants: $\left\{\begin{matrix} 0\bar{1}0 \\ \bar{1}00 \\ 001 \end{matrix}\right\}$

The Oxime, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}N{\cdot}OH$.—This derivative is conveniently prepared by mixing the solution of the aldehyde (1·5 grams) in a little methyl alcohol with a concentrated solution of hydroxylamine hydrochloride (2 grams) and sodium acetate (2 grams) and heating on the water-bath for half an hour, when on keeping starry groups of needles separate. Water is added, the precipitate collected, washed, and recrystallised from methyl alcohol:

0·3021 gave 19·9 c.c. N_2 at 13° and 758 mm. N = 7·8.

$C_9H_9O_3N$ requires N = 7·8 per cent.

5:6-*Methylenedioxy*-o-*tolualdoxime* melts at 144—145°, is readily soluble in methyl alcohol, and separates from this solvent in colourless, starry groups.

The *semicarbazone*, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, separates as a voluminous precipitate when a concentrated solution of semicarbazide hydrochloride and sodium acetate is added to the methyl-alcoholic solution of the aldehyde. It was collected and recrystallised from alcohol, in which it is sparingly soluble:

0·1169 gave 18·2 c.c. N_2 at 9° and 763 mm. N = 18·8.

$C_{10}H_{11}O_3N_3$ requires N = 19·0 per cent.

5:6-*Methylenedioxy*-o-*tolualdehydesemicarbazone* has no definite melting point, and if rapidly heated decomposes at about 248°, but several degrees lower if the determination is slowly carried out.

The Phenylhydrazone, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$. — In order to prepare this derivative the methyl-alcoholic solution of the aldehyde was mixed with excess of phenylhydrazine, and after boil-

ing for a few seconds the solution was cooled and well stirred, when the phenylhydrazone separated as a voluminous, crystalline mass. This was collected, dried on porous porcelain, and purified by recrystallisation from a mixture of benzene and light petroleum, from which it separated in colourless, prismatic needles:

0·1779 gave 16·9 c.c. N_2 at 11° and 764 mm. N = 11·2.

$C_{15}H_{14}O_2N_2$ requires N = 11·0 per cent.

5:6-*Methylenedioxy-o-tolualdehydephenylhydrazone* melts at 106° and is readily soluble in most organic solvents, but sparingly so in light petroleum. It is coloured intense yellow by concentrated hydrochloric acid, and the yellow substance thus produced is evidently an indole derivative, since it gives the chip reaction. Concentrated sulphuric acid also dissolves the phenylhydrazone with a deep yellowish-brown colour which deepens on keeping.

Oxidation of the Aldehyde to 5:6-*Methylenedioxy-o-toluic Acid*, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$.—This oxidation is readily carried out by dissolving the aldehyde (1 gram) in acetone (20 c.c.) and water (20 c.c.) at 50° and adding finely powdered permanganate (0·8 gram) in small quantities at a time. When the oxidation is complete the acetone and unchanged aldehyde are removed by distillation in a current of steam, the filtrate from the manganese precipitate concentrated and acidified, when a voluminous, chalky precipitate separates.

This is collected and recrystallised from acetic acid, from which the acid separates in glistening, flat needles melting at 217—218° and is identical with 5:6-methylenedioxy-*o*-toluic acid, the properties of which are described in detail on p. 917.

5:6:5′:6′-*Di-methylenetetraoxydi-o-methylstyryl Ketone*, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_2Me{:}O_2{:}CH_2$.

This substance, which is perhaps the most characteristic of the derivatives of 5:6-methylenedioxy-o-tolualdehyde, is readily prepared under the following conditions: The aldehyde (0·5 gram), dissolved in warm methyl alcohol (5 c.c.), is mixed with acetone (0·5 c.c.), two drops of potassium hydroxide (50 per cent.) are then added, and the deep yellow solution is heated to boiling for thirty seconds. The liquid clouds and deposits an oil which rapidly crystallises, and the mass is then digested with methyl alcohol to remove the more readily soluble 5:6-methylenedioxy-*o*-methylstyryl methyl ketone, which was not further examined. The deep yellow residue may then be conveniently crystallised either from acetone or benzene:

0·1069 gave 0·2819 CO_2 and 0·0502 H_2O. C = 71·9; H = 5·2.

$C_{21}H_{18}O_5$ requires C = 72·0; H = 5·2 per cent.

This brilliant yellow substance is characterised by the fact that the merest trace dissolves in acetic acid with a yellow colour, and on the addition of sulphuric acid a most intense methylene-blue solution is produced which soon becomes reddish-violet. When two drops of water are added, this changes to deep permanganate and dilution with an equal volume of water produces a bluish-violet solution. It melts at 183°, is sparingly soluble in methyl alcohol, almost insoluble in light petroleum, and not very readily soluble in acetone, but it dissolves freely in chloroform or acetic acid. The solution in boiling acetone deposits the substance in needles, whereas it separates from benzene in stout, striated prisms, and both modifications become opaque in the steam-oven.

Phenyl 5:6-*Methylenedioxy*-o-*methylstyryl Ketone*, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_5$.

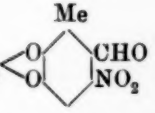
This characteristic substance was prepared by adding methyl-alcoholic potassium hydroxide (0·5 c.c. of 25 per cent.) to a cold solution of the aldehyde (1 gram) and acetophenone (1 gram) in methyl alcohol (10 c.c.).

After remaining for twenty-four hours the mass of glistening, pale yellow prisms, which had separated as a crust, was collected and recrystallised from methyl alcohol:

0·1044 gave 0·2924 CO_2 and 0·0509 H_2O. C = 76·4; H = 5·4.

$C_{17}H_{14}O_3$ requires C = 76·7; H = 5·3 per cent.

This substance melts at 110—111° and is sparingly soluble in methyl alcohol even on boiling; the solution of a trace in acetic acid gives, with sulphuric acid, an intense carmine solution.

3-*Nitro*-5:6-*methylenedioxy*-o-*tolualdehyde*, 

In preparing this nitro-derivative, 5:6-methylenedioxy-*o*-tolualdehyde (4 grams) was mixed with ordinary concentrated nitric acid (20 c.c.) and then cautiously warmed, when the aldehyde dissolved completely and soon the nitro-derivative commenced to separate as a voluminous mass of crystals. After adding water the sulphur-yellow mass was collected, well washed, and crystallised from dilute acetone, from which it separated in long, slender needles:

0·1095 gave 0·2066 CO_2 and 0·0339 H_2O. C = 51·5; H = 3·4.

0·2215 „ 12·6 c.c. N_2 at 14° and 766 mm. N = 6·7.

$C_9H_7O_5N$ requires C = 51·6; H = 3·3; N = 6·7 per cent.

3-*Nitro*-5 : 6-*methylenedioxy*-o-*tolualdehyde* melts at 122° and is readily soluble in benzene, acetone, or acetic acid, not so readily in methyl alcohol, and sparingly so in light petroleum. The solution in acetic acid gives, on the addition of sulphuric acid, a brilliant, cherry-red coloration. When the solution of the nitro-aldehyde in acetone is mixed with a drop of dilute sodium hydroxide and after remaining for a few minutes is diluted with an equal volume of water and gently warmed, it immediately turns blue, an indigo-blue precipitate separates, and the liquid is deep brown.

After collection, the precipitate—doubtless dimethylenetetraoxydimethylindigotin—was washed with water and then with acetone, and after drying on porous porcelain was a flaky, deep blue mass which did not exhibit a coppery lustre. The yield appeared to be almost quantitative. When the mother liquors from the crystallisation of the nitro-aldehyde were concentrated and mixed with water a considerable second crop separated, which melted at 118—120° and consisted of the 3-nitro-aldehyde. The filtrate from this crop, precipitated by water, yielded only a small third crop, which was viscid and melted at 80°. This, after two crystallisations from benzene and light petroleum, melted at 118—120° and consisted of the 3-nitro-aldehyde; it is therefore evident that if any isomeride was present it can only have been in very small quantity.

Oxidation of the 3-*Nitro-aldehyde to* 3-*Nitro*-5 : 6-*methylenedioxy*-o-*toluic Acid*, $CH_2{:}O_2{:}C_6HMe(NO_2)\cdot CO_2H$.—In carrying out this oxidation the nitro-aldehyde (1 gram) dissolved in acetone (20 c.c.) was gradually mixed at the ordinary temperature with very finely powdered permanganate (0·5 gram) and so soon as the pink colour had completely disappeared the whole was filtered and the black mass washed thoroughly with acetone. The residue was then extracted with hot water, the deep yellow solution acidified and allowed to remain, when long needles separated. After recrystallisation from water this acid melted at 186—187° and was identical with the 3-nitro-5 : 6-methylenedioxy-*o*-toluic acid described on p. 912, since a mixture of the two specimens melted at 186—187°.

3-*Nitro*-5 : 6-*methylenedioxy*-o-*tolualdehydedimethylacetal*,

$$CH_2{:}O_2{:}C_6HMe(NO_2)\cdot CH(OMe)_2.$$

—This substance was obtained under the following conditions *:

* The facility with which this dimethylacetal forms is remarkable, and the following observations were made in connexion with this matter:

The nitro-aldehyde, after twice crystallising from dilute acetone, separated unchanged, when its solution in boiling methyl alcohol was allowed to cool. The pure aldehyde, after boiling with alcohol and a few drops of sulphuric acid for some minutes, separated on cooling unchanged, and the same thing happened when the aldehyde was crystallised from alcohol containing a

The nitro-aldehyde, prepared as just described, after washing with water and draining on porous porcelain, but which doubtless still contained a trace of nitric acid, was recrystallised from methyl alcohol, when glistening, well-developed, lemon-yellow prisms separated and melted at 103—104°:

0·1006 gave 0·1907 CO_2 and 0·0458 H_2O. C = 51·7; H = 5·1.
0·2206 „ 10 c.c. N_2 at 15° and 766 mm. N = 5·4.
$C_{11}H_{13}O_6N$ requires C = 51·7; H = 5·1; N = 5·5 per cent.

This dimethylacetal crystallises with great facility. It dissolves readily in chloroform or benzene, and separates, on the addition of light petroleum (in which it is very sparingly soluble), in glistening, pale yellow, prismatic needles. It is readily soluble in acetic acid, and the addition of sulphuric acid produces a brilliant, cherry-red coloration.

Conversion of 5:6-*Methylenedioxy-o-toluic Acid into* 3-*Nitro*-5:6-*methylenedioxy-o-toluic Acid*, $CH_2{:}O_2{:}C_6HMe(NO_2)\cdot CO_2H$, *and Dinitro*-2:3-*methylenedioxytoluene*, $CH_2{:}O_2{:}C_6HMe(NO_2)_2$. — 5:6-Methylenedioxy-*o*-toluic acid (p. 916) is sparingly soluble in cold concentrated nitric acid, but on gently warming it becomes yellow, passes into solution, slight effervescence takes place, and the nitro-acid soon begins to separate in needles. After twenty-four hours water is added, the mass of crystals collected, washed thoroughly, and stirred with excess of dilute sodium carbonate, when a small quantity of a yellow substance remains undissolved. This is collected and crystallised from methyl alcohol, from which it separates in starry groups of pale lemon plates:

0·1100 gave 0·1721 CO_2 and 0·0273 H_2O. C = 42·5; H = 2·6.
0·1334 „ 13·8 c.c. N_2 at 12° and 763 mm. N = 12·3.
$C_8H_6O_6N_2$ requires C = 42·6; H = 2·7; N = 12·4 per cent.

Dinitro-2:3-*methylenedioxytoluene* melts at 132°, is readily soluble in benzene, chloroform, ethyl acetate, or acetone, but sparingly so in light petroleum, and crystallises well from a mixture of benzene or chloroform with light petroleum. The solution in acetic acid gives on the addition of sulphuric acid a yellowish-green coloration, which becomes pure yellow when a few drops of water are added.

The yellow solution of the sodium salt which had been separated from the above substance was acidified with hydrochloric acid, when a milky liquid was produced which on stirring soon crystallised.

little nitric acid. When, however, a drop of nitric acid was added to the warm solution of the aldehyde in methyl alcohol and the whole boiled for half a minute, the dimethylacetal separated on cooling. From these observations it would seem (i) that the dimethylacetal forms much more readily than the diethylacetal and, (ii) that traces of nitric acid may prove valuable in bringing about the combination of aldehydes with alcohols.

The precipitate was collected and recrystallised from water, from which the nitro-acid separated in stout, prismatic needles:

0·3215 gave 16·2 c.c. N_2 at 10° and 760 mm. N = 6·1.

$C_9H_7O_6N$ requires N = 6·2 per cent.

Titration: 0·2754 neutralised 12·2 c.c. *N*/10-NaOH, and this amount of a monobasic acid, $C_9H_7O_6N$, should neutralise 12·2 c.c. When this solution was acidified and allowed to remain the nitro-acid gradually separated in long, thin plates which were almost colourless.

3-*Nitro*-5:6-*methylenedioxy*-o-*toluic acid* softens somewhat at 180° and melts at 186—187° without effervescence. It dissolves moderately readily in glacial acetic acid, and the solution gives, on the addition of sulphuric acid, a most intense sage-green coloration which becomes yellow on the addition of water or a drop of nitric acid.

Proof of the Constitution of 5:6-*Methylenedioxy*-o-*tolualdehyde.*

That the aldehyde (m. p. 75°) obtained by the oxidation of anhydrotetrahydromethylcryptopine has this constitution was proved by conversion into the derivatives described below (compare p. 823).

5:6-*Carbonyldioxy*-o-*tolualdehyde*, $CO{:}O_2{:}C_6H_2Me{\cdot}CHO$.—In preparing this substance 5:6-methylenedioxy-*o*-tolualdehyde (1 gram) was heated with phosphorus pentachloride (3·8 grams) at 105° for an hour in such a way that the phosphorus trichloride distilled off as it formed, and then the temperature was raised to 130° for a couple of minutes.

The yellow product was mixed with formic acid (2 c.c. of D 1·22) and allowed to remain in the ice-chest, when a crystalline substance separated which melted at 103—104° and the melting point was not changed by recrystallisation from the same solvent:

0·1157 gave 0·2576 CO_2 and 0·0360 H_2O. C = 60·7; H = 3·4.

$C_9H_6O_4$ requires C = 60·7; H = 3·3 per cent.

5:6-*Dihydroxy*-o-*tolualdehyde* (*Methylprotocatechualdehyde*), $(OH)_2C_6H_2Me{\cdot}CHO$.—The carbonyl derivative just described dissolves readily when boiled with water, and the solution, after concentration by distillation under diminished pressure, deposits pale drab needles which evidently contain water of crystallisation, since they become opaque on drying in the steam-oven:

0·1113 gave 0·2575 CO_2 and 0·0530 H_2O. C = 63·1; H = 5·3.

$C_8H_8O_3$ requires C = 63·2; H = 5·3 per cent.

5:6-*Dihydroxy*-o-*tolualdehyde* melts at about 168° and is sparingly soluble in cold, but readily so in hot, water. It is readily

soluble in methyl alcohol, rather less so in ether, and is sparingly soluble even in boiling benzene; it separates from the latter solution on cooling in microscopic, striated, leafy crystals. It dissolves readily in dilute sodium hydroxide to a yellow solution which does not rapidly darken when shaken with air, and on acidifying the aldehyde separates as a voluminous, colourless, crystalline mass. The aqueous solution gives, on the addition of ferric chloride, an intense green coloration which becomes reddish-brown on adding ammonium carbonate.

The *semicarbazone*, $(OH)_2C_6H_2Me\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, soon begins to separate in prismatic needles when excess of a concentrated solution of semicarbazide hydrochloride and sodium acetate is added to the warm saturated solution of the dihydroxy-aldehyde. It begins to darken at about 210° and decomposes with effervescence at about 230°:

0·1061 gave 18·4 c.c. N_2 at 19° and 758 mm. N = 19·9.
$C_9H_{11}O_3N_3$ requires N = 20·1 per cent.

The *oxime*, $(OH)_2C_6H_2Me\cdot CH{:}N\cdot OH$, was prepared by adding a concentrated aqueous solution of hydroxylamine hydrochloride and sodium acetate to the warm concentrated solution of the dihydroxy-aldehyde.

It separates in long needles which closely resemble the aldehyde in appearance and, like this substance, it becomes opaque in the water-oven. It has no definite melting point, but decomposes with effervescence at about 180—185° to a black froth extending up the capillary tube:

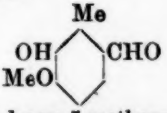
0·2102 gave 14·9 c.c. N_2 at 19° and 758 mm. N = 8·0.
$C_8H_9O_3N$ requires N = 8·4 per cent.

Methylation of 5:6-*Dihydroxy*-o-*tolualdehyde*.—In the first experiment the pure aldehyde (1·5 grams) was dissolved in a solution of sodium (0·6 gram) in methyl alcohol in a coal-gas atmosphere, methyl sulphate (5 grams) was then added, and the whole heated just to boiling on the water-bath. On the addition of water an oil separated which soon crystallised, and after collecting, washing with water, and drying on porous porcelain the substance separated from methyl alcohol, in which it is readily soluble, in glistening plates like naphthalene. For analysis the substance was crystallised from water, in which it is sparingly soluble and from which it separates, in glistening, striated, four-sided plates:

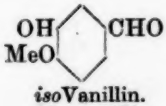
0·1032 gave 0·2457 CO_2 and 0·0567 H_2O. C = 64·9; H = 6·1.
$C_9H_{10}O_3$ requires C = 65·0; H = 6·0 per cent.

It is worthy of note that in the above methylation, although more than the calculated quantity of sodium necessary for the

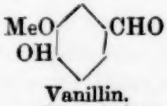
formation of the disodium derivative of the dihydroxy-aldehyde (0·46 gram) was employed, the product obtained consisted almost entirely of this monomethyl ether. It is probable that it is the hydroxy-group adjacent to the methyl group which, owing to steric hindrance, has escaped methylation, and that the monomethyl ether is the 5-methyl ether corresponding with *iso*vanillin, and not with vanillin:



6-Hydroxy-5-methoxy-*o*-tolualdehyde.



*iso*Vanillin. M. p. 117°.



Vanillin. M. p. 81°.

This view is borne out by the comparatively high melting point, the other physical properties, and by the fact that the substance is odourless in the cold, and even when heated has only a faint odour of vanilla. 6-*Hydroxy*-5-*methoxy*-o-*tolualdehyde* melts at 133—135° and is sparingly soluble in cold, but moderately readily so in hot, water. The cold aqueous solution gives only a faint green coloration with ferric chloride, but the addition of ferric chloride to the methyl-alcoholic solution produces a deep sage-green colour, which becomes deep reddish-violet when ammonium carbonate is added. It dissolves in dilute sodium hydroxide to a yellow solution and is reprecipitated on the addition of acids.

5:6-*Dimethoxy*-o-*tolualdehyde*, $(MeO)_2C_6H_2Me{\cdot}CHO$.—In order to complete the methylation of 5:6-dihydroxy-*o*-tolualdehyde, it was treated with sodium methoxide and methyl sulphate as described in the above preparation of the monomethyl ether, and, after the alternate addition of sodium methoxide and methyl sulphate had been repeated four times, the product was mixed with water, rendered alkaline by the addition of sodium hydroxide, and extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, and evaporated, when a purple syrup was obtained which gradually crystallised. After remaining in contact with porous porcelain, which removed much of the purple impurity, the still highly coloured mass was extracted with boiling light petroleum, in which the purple substance is insoluble, and on filtering and concentrating considerably the solution deposited, especially on rubbing, a colourless mass of felted needles:

0·1129 gave 0·2760 CO_2 and 0·0697 H_2O. C = 66·7; H = 6·8.

$C_{10}H_{12}O_3$ requires C = 66·7; H = 6·7 per cent.

5:6-*Dimethoxy*-o-*tolualdehyde* melts at 52—53° and, especially when warmed, has an odour similar to that of vanillin methyl ether (veratraldehyde, $(MeO)_2C_6H_3{\cdot}CHO$ (m. p. 42°). It is sparingly soluble in cold light petroleum (b. p. 60—80°), but much more

readily so on boiling, and if the solution is dilute and is slowly cooled it separates in long, slender, glistening needles. It is very readily soluble in most other organic solvents, and distils without decomposition.

The Oxime, $(MeO)_2C_6H_2Me\cdot CH{:}N\cdot OH$.—This derivative was obtained by dissolving the dimethoxy-aldehyde (1 gram) in methyl alcohol and adding a concentrated aqueous solution of hydroxylamine hydrochloride (1 gram) and sodium acetate (1 gram), when after boiling for a few minutes and leaving in the ice-chest part of the oxime separated in long, flat needles and the remainder was precipitated by adding water. It was recrystallised from methyl alcohol, from which it separates in glistening needles:

0·1436 gave 9 c.c. N_2 at 15° and 766 mm. N = 7·4.

$C_{10}H_{13}O_3N$ requires N = 7·2 per cent.

5:6-*Dimethoxy-o-tolualdoxime* melts at 98—99° and is readily soluble in most organic solvents, but sparingly so in cold light petroleum. It is somewhat soluble in boiling water and, on cooling, the solution clouds and then deposits the oxime in groups of slender needles.

The Semicarbazone, $(MeO)_2C_6H_2Me\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$.—When a concentrated aqueous solution of semicarbazide hydrochloride and sodium acetate was added to the solution of the dimethoxy-aldehyde in boiling methyl alcohol a satiny, crystalline precipitate separated on keeping, which was collected and recrystallised from alcohol:

0·1159 gave 16·8 c.c. N_2 at 14° and 766 mm. N = 17·2.

$C_{11}H_{15}O_3N_3$ requires N = 17·7 per cent.

5:6-*Dimethoxy-o-tolualdehydesemicarbazone* shrinks at 215° and melts at 220° without appreciable decomposition; it is sparingly soluble in boiling alcohol, and separates on cooling in glistening plates like benzoic acid.

Section IV.

5:6-*Methylenedioxy-o-toluic Acid* (*Methylpiperonylic Acid*), $CH_2{:}O_2{:}C_6H_2Me\cdot CO_2H$.

This acid, together with some 4:5-dimethoxyhomophthalic acid, $(MeO)_2C_6H_2(CO_2H)\cdot CH_2\cdot CO_2H$, was obtained as an ochreous or brown, chalky precipitate (*C*) from the product of the oxidation of anhydrotetrahydromethylcryptopine in the manner described on p. 901. For the purpose of purification it was first dissolved in a slight excess of dilute sodium carbonate, boiled with animal charcoal, reprecipitated, and the now much cleaner acid dissolved in excess of dilute ammonia, mixed with barium chloride, and gently boiled for half an hour. The small quantity of the insoluble barium salt of 4:5-dimethoxyhomophthalic acid (p. 922) was removed by

filtration, the 5:6-methylenedioxy-*o*-toluic acid precipitated by hydrochloric acid, and recrystallised either from dilute acetic acid or from acetone:

0·1048 gave 0·2301 CO_2 and 0·0432 H_2O. C=59·9; H=4·5.
0·1244 „ 0·2729 CO_2 „ 0·0506 H_2O. C=59·8; H=4·5.
$C_9H_8O_4$ requires C=60·0; H=4·4 per cent.

5:6-*Methylenedioxy-o-toluic acid* melts at 215—216°, is readily soluble in acetic acid or acetone, and crystallises from these solvents in groups of glistening needles. It is almost insoluble in cold, but appreciably so in boiling, water, and separates on cooling in woolly masses. It dissolves rather sparingly in methyl alcohol, and still less so in ether or light petroleum, but it is moderately soluble in benzene and may be crystallised from this solvent.

When carefully heated in small quantities it sublimes without decomposition, yielding a sublimate very like naphthalene in appearance. The solution of a trace of the acid in a drop of glacial acetic acid gives on the addition of sulphuric acid at first a yellow solution, but the colour gradually changes to an intense cherry-red. If a trace of the acid is evaporated with a drop of nitric acid on a watch-glass the yellow residue dissolves in ammonia, producing a cherry-red solution.

The Methyl Ester, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2Me$.—The acid does not appear to be readily esterified by the usual methods, such as boiling with alcohol and sulphuric acid, probably because of the steric hindrance exerted by the methyl group, and the methyl ester was therefore prepared in the following way. The acid (1 gram) was mixed with phosphorus trichloride (1 gram), and after a few minutes the clear liquid was heated in boiling water for five minutes when it separated into two layers, the upper of which was the acid chloride, and soon solidified to a buttery mass. The whole was mixed with methyl alcohol, heated to boiling for ten minutes, and then poured into water, when an oil separated which gradually crystallised. After collecting and washing thoroughly with dilute sodium carbonate, which removes an appreciable quantity of unesterified acid, the crystalline residue was purified by recrystallisation from dilute methyl alcohol, from which it separated as a voluminous, woolly mass of needles:

0·1093 gave 0·2481 CO_2 and 0·0513 H_2O. C=61·9; H=5·2.
$C_{10}H_{10}O_4$ requires C=61·9; H=5·1 per cent.

Methyl 5:6-*methylenedioxy-o-toluate* melts at 52—53° and dissolves readily in the usual organic solvents; it may be conveniently crystallised from light petroleum, from which it separates in stellate groups of colourless laminæ.

Dibromo-2:3-*methylenedioxytoluene*, $CH_2{:}O_2{:}C_6HBr_2Me$. — The

gradual addition of bromine water (containing 1 c.c. of bromine) to the well-cooled solution of 5:6-methylenedioxy-*o*-toluic acid (1·5 grams) in water and sodium carbonate (4 grams) causes an immediate milkiness and in a short time a chalky precipitate separates. This was collected, washed, dried, and crystallised from methyl alcohol:

0·1456 gave 0·1866 AgBr. Br = 54·5.

$C_8H_6O_2Br_2$ requires Br = 54·4 per cent.

Dibromo-2:3-methylenedioxytoluene melts at 84—85°, and has, especially when warmed, an odour reminiscent of that of the higher dibromides of the aliphatic series; it distils under diminished pressure without decomposition, and is volatile with difficulty in steam. It is readily soluble in boiling methyl or ethyl alcohols, but much less so in the cold, and separates in colourless needles; it is also very readily soluble in benzene, light petroleum, chloroform, or acetic acid. The solution in a little acetic acid gives, on the addition of much sulphuric acid, an intense crimson solution which on keeping becomes brown and then green, and the green colour develops rapidly on the addition of a few drops of water.

5:6-*Carbonyldioxy-o-toluic Acid*, $CO{:}O_2{:}C_6H_2Me{\cdot}CO_2H$.—This substance and its derivatives were prepared by a series of reactions similar to those described by Barger (T., 1908, **93**, 568). 5:6-Methylenedioxy-*o*-toluic acid (3 grams) was heated with phosphorus pentachloride (11 grams) for three hours in a small fractionating flask in such a way that the phosphoryl chloride distilled off as it was produced; the product was then fractionated, when almost the whole quantity distilled at 165°/15 mm. as a heavy, colourless oil which on cooling solidified to a buttery mass of the impure dichloro-acid chloride, $CCl_2{:}O_2{:}C_6H_2Me{\cdot}COCl$.

This was mixed with three volumes of anhydrous formic acid, when a heavy, white powder soon formed which dissolved on boiling and separated on keeping in the ice-chest as a mass of crystals consisting of 5:6-carbonyldioxy-*o*-toluic acid. The same substance is obtained by melting the crude, buttery trichloride under water at about 50°, when the oil gradually changes and becomes quite hard and crystalline. For analysis the substance was recrystallised from formic acid, in which it is rather sparingly soluble, and from which it separates in flat needles or clusters of striated prisms:

0·1198 gave 0·2446 CO_2 and 0·0343 H_2O. C = 55·7; H = 3·2.

$C_9H_6O_5$ requires C = 55·7; H = 3·1 per cent.

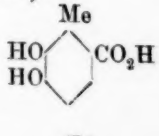
5:6-*Carbonyldioxy-o-toluic acid* has no definite melting point; it softens somewhat above 200°, and melts roughly at 260° to a brown oil.

5:6-*Dihydroxy-o-toluic Acid* (*Methylprotocatechuic Acid*), $(OH)_2C_6H_2Me\cdot CO_2H$.

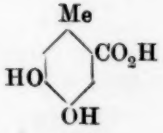
—The recrystallised carbonyldioxy-acid just described is sparingly soluble in water and only slowly decomposed on boiling with water, but if the acid is ground to a fine paste with much water and the solution boiled, decomposition soon sets in with evolution of carbon dioxide, and the acid gradually passes into solution. After concentrating considerably by distilling off some of the water under diminished pressure, the solution on keeping in the ice-chest deposited starry groups of the pure dihydroxy-acid, and these did not appear, like protocatechuic acid, to contain water of crystallisation, since they did not become opaque on drying at 90°:

0·1119 gave 0·2330 CO_2 and 0·0486 H_2O. C = 56·8; H = 4·8.
0·1179 „ 0·2473 CO_2 „ 0·0515 H_2O. C = 57·2; H = 4·8.
$C_8H_8O_4$ requires C = 57·1; H = 4·8 per cent.

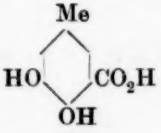
5:6-*Dihydroxy-o-toluic acid*, when rapidly heated, decomposes at about 200—202° with evolution of gas. It is readily soluble in hot, but rather sparingly so in cold, water, and the aqueous solution gives with ferric chloride a deep green coloration which changes to crimson on the addition of ammonium carbonate. Like protocatechuic acid, it is almost insoluble in benzene, dissolves rather readily in ether, and more readily still in methyl alcohol. The solution of the ammonium salt reduces ammoniacal silver nitrate instantly in the cold, but, unlike protocatechuic acid, the dilute aqueous solution is not precipitated by lead acetate. The addition of methyl-alcoholic potassium hydroxide to the solution of the acid in methyl alcohol gives at first a slight green coloration, and in contact with air this becomes yellow, then deep claret, and a sparingly soluble potassium salt separates which dissolves in water to a deep claret solution, becoming yellow on the addition of hydrochloric acid. 5:6-Dihydroxy-*o*-toluic acid (I) does not appear to have been previously described. It is isomeric with berberinic acid (m. p. 165°, II), which is obtained when berberine is fused with potassium hydroxide (Hlasiwetz and Gilm, *Jahresber.*, 1864, 407; Perkin, T., 1889, **55**, 88), with homocatecholcarboxylic acid (m. p. 204°, III), obtained by oxidising *p*-homosalicylic acid, $OH\cdot C_6H_3Me\cdot CO_2H$, with potassium persulphate (D.R.-P., 81, 298), and with homoprotocatechuic acid (m. p. 127°, IV; compare Tiemann and Nagai, *Ber.*, 1877, **10**, 207):



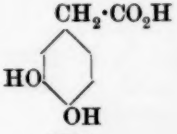
(I.)



(II.)



(III.)



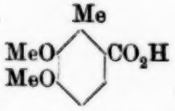
(IV.)

iso*Homocatechol* (2:3-*Dihydroxytoluene*), $MeC_6H_3(OH)_2 = 1:2:3$. —When 5:6-dihydroxy-*o*-toluic acid is heated under diminished pressure some carbon dioxide is eliminated, and if the residue is distilled a good deal of charring takes place, and the distillate consists largely of unchanged acid, and does not appear to contain more than traces of the corresponding dihydroxytoluene. It was subsequently found that the decomposition proceeds much more smoothly when the solution of the acid (2 grams) in water (20 c.c.) is heated in a sealed tube at 170—180° for five hours. The product, which was only slightly discoloured, was freed from water by distillation from the water-bath under diminished pressure, and the residue rapidly fractionated, when it passed over almost completely at 136—137°/14 mm. or 238—240° under the ordinary pressure, and in both cases crystallised on keeping:

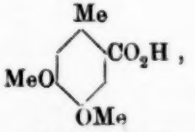
0·1673 gave 0·4111 CO_2 and 0·0992 H_2O. C = 67·0; H = 6·6.
$C_7H_8O_2$ requires C = 67·8; H = 6·4 per cent.

The determination of the melting point of this substance was difficult owing to the small amount available, but the value observed was 40—43°; it is very readily soluble in water, and the solution gives with ferric chloride a transient, green coloration which almost instantly changes to brown, and the addition of ammonium carbonate produces a reddish-violet solution. These properties leave no doubt that the substance is *iso*homocatechol, which Limpach (*Ber.*, 1891, **24**, 4137) obtained by the hydrolysis of the methyl ether, $MeC_6H_3(OMe)OH = 1:2:3$, which results from the action of nitrous acid on 3-amino-*o*-tolyl methyl ether, $MeC_6H_3(OMe)\cdot NH_2$. Limpach states that *iso*homocatechol melts at 47°, distils at 238—240°, and gives the characteristic reaction with ferric chloride, which is described above. That the substance is not homocatechol, $MeC_6H_3(OH)_2 = 1:3:4$, is clear from a comparison of properties, since the latter melts at 51°, distils at 251—252° (Béhal, Desvignes, *Bull. Soc. chim.*, 1893, [iii], **9**, 144), and gives a lasting colour with ferric chloride. Confirmation of this view was obtained by mixing equal quantities of the two substances, when a syrup resulted which crystallised with difficulty in a freezing mixture.

5:6-*Dimethoxy-o-toluic Acid*.—This new acid (I), which is isomeric and closely allied with 4:5-dimethoxy-*o*-toluic acid (II), obtained by Perkin and Weizmann by the oxidation of the corre-



(I.) M. p. 177°.



(II.) M. p. 145°.

sponding aldehyde (T., 1906, **89**, 1651), is readily prepared under the following conditions: In a flask filled with coal gas 5:6-dihydroxy-*o*-toluic acid (1·6 grams) is added to the solution of sodium (1 gram) in methyl alcohol, methyl sulphate (5 grams) immediately poured in, and the whole heated on the water-bath for five minutes. Methyl-alcoholic potassium hydroxide (5 c.c. of 25 per cent.) is then added, the whole boiled for ten minutes in order to hydrolyse any methyl ester which may have been produced, diluted with water, and evaporated until free from methyl alcohol. On the addition of hydrochloric acid a voluminous, crystalline precipitate separates, which is collected, washed, and crystallised from acetic acid:

0·1182 gave 0·2645 CO_2 and 0·0623 H_2O. C = 61·0; H = 5·8.
0·1113 „ 0·2482 CO_2 „ 0·0616 H_2O. C = 60·8; H = 6·1.
$C_{10}H_{12}O_4$ requires C = 61·2; H = 6·1 per cent.

5:6-*Dimethoxy*-o-*toluic acid* melts, not quite sharply, at 177° and is very sparingly soluble in cold water, but the freshly precipitated acid dissolves appreciably in boiling water, and separates on cooling as a woolly mass of needles.

The Methyl Ester, $(MeO)_2C_6H_2Me{\cdot}CO_2Me$.—In order to prepare this derivative the acid (3 grams) was heated with excess of phosphorus trichloride (4 grams) until two layers had formed; the upper layer was then poured into methyl alcohol, and after heating to boiling for a few minutes water was added and the oily ester extracted with ether. The ethereal solution was well washed with sodium carbonate, dried, and the ether removed, when a colourless oil remained which showed no signs of crystallising. On distillation, this methyl ester passed over constantly at 168°/14 mm. as a colourless oil, which remained in this condition for nearly two months and then suddenly crystallised. The crystalline mass was left in contact with porous porcelain and then recrystallised from light petroleum:

0·1268 gave 0·2910 CO_2 and 0·0770 H_2O. C = 62·6; H = 6·7.
$C_{11}H_{14}O_4$ requires C = 62·8; H = 6·7 per cent.

Methyl 5:6-*dimethoxy*-o-*toluate* melts at 46—48° and is readily soluble in light petroleum, from which it separates in colourless needles; it is also readily soluble in most other organic solvents.

Oxidation of 5:6-*Dimethoxy*-o-*toluic Acid to Hemipinic Acid.*

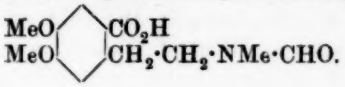
In order to obtain evidence as to the relative positions of the groups in this acid, the substance (2 grams), dissolved in dilute sodium carbonate, was oxidised by potassium permanganate (3 grams) at the temperature of the steam-bath, but even under these conditions oxidation did not take place readily. The product

was filtered, rendered acid to Congo paper by the addition of hydrochloric acid, and allowed to remain in the ice-chest for twenty-four hours, when 0·4 gram of a crystalline acid separated, which consisted mainly of unchanged dimethoxy-*o*-toluic acid. The filtrate from this acid was evaporated to dryness by distillation under diminished pressure, the residue mixed with sand, and extracted with ether in a Soxhlet apparatus. On evaporation, the ethereal solution deposited a syrup which rapidly crystallised, and the crystals were drained on porous porcelain, washed with ether, and recrystallised from water, when the colourless needles, which became opaque on drying in the water-oven, melted at about 180° with effervescence, and consisted of hemipinic acid. (Found, C = 53·0; H = 4·4. $C_{10}H_{10}O_6$ requires C = 53·1; H = 4·4 per cent.)

Titration: 0·2156 required for neutralisation 19·0 c.c. *N*/10-NaOH, whereas this amount of a dibasic acid, $C_{10}H_{10}O_6$, should neutralise 19·1 c.c. To complete the proof that this acid was hemipinic acid, it was dissolved in water, mixed with excess of ethylamine, and, after evaporating to dryness, the salt was distilled in a test-tube, and the crude distillate crystallised from methyl alcohol, from which it separated in colourless needles melting at 87—88°, the melting point of the ethylimide of hemipinic acid.

2-Carboxy-4:5-dimethoxyphenylacetic Acid (*4 : 5-Dimethoxyhomophthalic Acid*), $(MeO)_2C_6H_2(CO_2H)\cdot CH_2\cdot CO_2H$.—It is mentioned on p. 916 that an insoluble barium salt was obtained during the purification of 5:6-methylenedioxy-*o*-toluic acid, and this, on examination, has been found to be the barium salt of the above acid. The barium salt, collected from several operations, was warmed with dilute hydrochloric acid, when an acid separated which crystallised from acetone, in which it is very sparingly soluble, in minute, felted needles melting at 214—215°. (Found, C = 55·1; H = 5·2. $C_{11}H_{12}O_6$ requires C = 55·0; H = 5·0 per cent.) On titration, 0·2174 neutralised 18·1 c.c. *N*/10-NaOH, which is the amount required to neutralise this weight of a dibasic acid, $C_{11}H_{12}O_6$. This acid is very sparingly soluble even in boiling water, separates in slender needles, and has all the properties of 2-carboxy-4:5-dimethoxyphenylacetic acid, which was first obtained from trimethylbrazilin by oxidation with permanganate (Perkin, T., 1902, **81**, 1028), and was subsequently synthesised from 5:6-dimethoxy-1-hydrindone (Perkin and Robinson, T., 1907, **91**, 1082). The identity of the acid from anhydrotetrahydromethylcryptopine with that obtained from trimethylbrazilin was proved by careful comparison, and by the fact that the mixture of the two preparations melted at 214—215°.

N-*Formyl*-4:5-*dimethoxy*-2-*β*-*methylaminoethylbenzoic Acid*,



During the working up of the product of the oxidation of anhydrotetrahydromethylcryptopine (p. 900) an ethereal extract was obtained (*D*) which, on examination, was found to contain the above acid, together with 5:6-methylenedioxy-*o*-toluic acid (p. 901) and *m*-hemipinic acid. The separation of these acids, which could not be satisfactorily brought about by recrystallisation, was ultimately accomplished in the following manner: The crude, brown, viscid mass was dissolved in excess of dilute ammonia, mixed with barium chloride, and boiled for fifteen minutes, when the insoluble barium salt of *m*-hemipinic acid separated in quantity and was collected and thoroughly washed. This salt dissolved readily in hot dilute hydrochloric acid and, on cooling, a woolly mass of needles separated which melted at 200—202° and consisted of *m*-hemipinic acid. On titration, 0·5008 required 43·9 c.c. *N*/10-NaOH for neutralisation, whereas this amount of a dibasic acid, $C_{10}H_{10}O_6$, should neutralise 44·2 c.c. The identity was further confirmed by conversion into the ethylimide, which melted at 226—228°. The ammoniacal filtrate from the barium salt of this acid was digested with animal charcoal for several hours, and in this way much of the brown colouring matter was removed, the filtrate was mixed with a considerable excess of hydrochloric acid and left in the ice-chest for ten days, when a voluminous mass of crystals gradually formed. This was collected and subjected to repeated fractional crystallisation from water, by which means it was separated into a comparatively small quantity of 5:6-methylenedioxy-*o*-toluic acid (m. p. 215—216°) and the new acid.

N-*Formyl*-4:5-*dimethoxy*-2-*β*-*methylaminoethylbenzoic acid* melts at 153° and separates from water, in which it is rather sparingly soluble, in the cold, but readily so on boiling, as a felted mass of colourless needles:

0·1354 gave 0·2881 CO_2 and 0·0785 H_2O. C = 58·3; H = 6·4.
0·4634 „ 21·3 c.c. N_2 at 16° and 763 mm. N = 5·4.
$C_{13}H_{17}O_5N$ requires C = 58·4; H = 6·4; N = 5·2 per cent.

Titration: 0·2816, dissolved in water, neutralised 10·8 c.c. *N*/10-NaOH, whereas this amount of a monobasic acid, $C_{13}H_{17}O_5N$, should neutralise 10·6 c.c. As it was thought that boiling with alkali might eliminate the formyl group, and thus double the amount of alkali neutralised, a large excess was added, and after boiling for ten minutes the excess titrated back, but the alkali

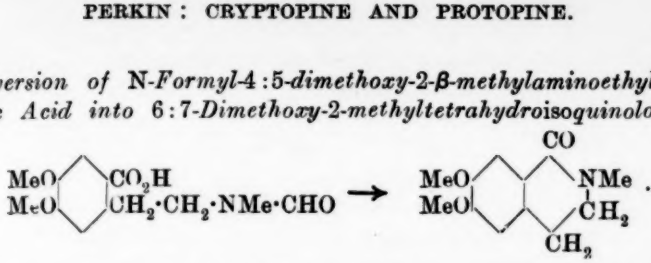
neutralised was only 10·9 c.c., and therefore hydrolysis had not taken place. This formyl acid is rather sparingly soluble in methyl alcohol, acetone, or chloroform in the cold and very sparingly so in cold ether or benzene. It crystallises from much ether in colourless crusts, and from methyl alcohol or acetone in groups of needles. It is not acted on by acetic anhydride, crystallises unchanged from an aqueous solution of semicarbazide acetate, and forms salts both with alkalis and acids. The slightly alkaline, rather dilute solution of the ammonium salt gives, with silver nitrate, an amorphous precipitate which is very difficult to filter and, with copper sulphate, no precipitate in the cold, but a pale green, amorphous precipitate separates on boiling; lead acetate produces a heavy, white, amorphous precipitate, and the barium and calcium salts are readily soluble.

Formyldimethoxymethylaminoethylbenzoic acid forms salts with concentrated mineral acids, which dissociate in contact with much water. Thus it dissolves in concentrated sulphuric acid and, on adding twice the volume of water and leaving in the ice-chest, a granular sulphate separates which melts at about 183—185° to a colourless syrup and dissolves in water, but the solution immediately deposits a crystalline precipitate which melts at 153° and consists of the formyl acid. The same salt is obtained as a crystalline crust when the concentrated solution of the acid in methyl alcohol is mixed with sulphuric acid and allowed to remain; the formation of the methyl ester of the acid does not occur under these conditions. The beautifully crystalline *hydrochloride*, $C_{13}H_{17}O_5N,HCl$, separates as a crystalline mass when the solution of the acid in boiling concentrated hydrochloric acid is allowed to remain, but is best prepared by saturating the warm concentrated solution of the acid in methyl alcohol with hydrogen chloride. The voluminous mass of needles, which separates on cooling, was rapidly collected, and dried over sulphuric acid in an atmosphere of hydrogen chloride:

0·1009 gave 0·0911 CO_2 and 0·0541 H_2O. C = 51·6; H = 5·6.
0·2213 „ 0·0958 AgCl. Cl = 10·7.
$C_{13}H_{17}O_5N,HCl$ requires C = 51·4; H = 5·6; Cl = 11·0 per cent.

The hydrochloride shrinks at about 170°, and effervesces and melts rather sharply at 183° to a colourless syrup. It is readily soluble in water, but the solution rapidly deposits a crystalline precipitate of the formyl acid, and the filtrate from this contains hydrochloric acid. The salt is also completely dissociated when it is heated in the steam-oven until the weight is constant, and the residual opaque mass, which melts at 150—153°, consists of the pure formyl acid. (Found, C = 58·1; H = 6·3 per cent.)

Conversion of N-*Formyl*-4:5-*dimethoxy*-2-β-*methylaminoethylbenzoic Acid into* 6:7-*Dimethoxy*-2-*methyltetrahydroisoquinolone*,



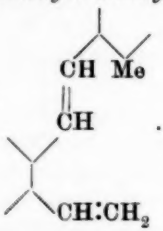
The formyl group in the above acid is very firmly attached; the acid is not appreciably decomposed when the solution in ten times the weight of water is heated at 140—150° for an hour, since the acid separates unchanged when the solution is concentrated. When, however, the acid (1 gram) was heated with 5 per cent. sulphuric acid (10 c.c.) at 150° for an hour, complete hydrolysis had taken place and, after exactly removing the sulphuric acid by barium hydroxide and evaporating, first to a small bulk on the water-bath and then completely over sulphuric acid in a desiccator, an almost colourless syrup remained, which gradually crystallised. The crystals were left in contact with porous porcelain and then recrystallised from ether, in which the substance is sparingly soluble and from which it separates in brilliant, colourless prisms melting at 126—127°:

0·1222 gave 0·2899 CO_2 and 0·0734 H_2O. C = 64·7; H = 6·8.
0·1165 „ 6·6 c.c. N_2 at 12° and 750 mm. N = 6·6.
$C_{12}H_{15}O_3N$ requires C = 65·1; H = 6·8; N = 6·3 per cent.

That this substance is 6:7-dimethoxy-2-methyltetrahydro*iso*quinolone, first prepared by Pyman (T., 1909, **95**, 1272), was proved by direct comparison and by the fact that the mixture of both preparations melted at 126—127°. The elimination of formic acid and formation of this substance also takes place when the dry formyl acid is heated. In this experiment the formyl acid (0·5401 gram) was heated in a test-tube in a sulphuric acid bath at 230°, when an acid liquid was given off, doubtless formic acid, and the loss in weight amounted to 0·0906 gram or 16·8 per cent., whereas the elimination of formic acid from $C_{13}H_{17}O_5N$ requires 17·1 per cent. The transparent resin remaining in the test-tube was dissolved in a little water, the solution allowed to evaporate in a desiccator, and the residue rubbed with a very little water, when a crystalline paste was produced which, in contact with porous porcelain, left a colourless crust. This separated from a few drops of water as a voluminous mass of slender needles, which, after drying, melted at 126—127° and consisted of 6:7-dimethoxy-2-methyltetrahydro*iso*quinolone.

Section V.

4:5-Dimethoxy-3′:4′-methylenedioxy-6′-methyl-2-vinylstilbene.

(Cryptopidene), 

This substance is produced, together with trimethylamine, by the action of methyl-alcoholic potassium hydroxide on anhydrotetrahydromethylcryptopine methosulphate. This methosulphate may be obtained in almost quantitative yield by stirring the base (1 gram) with methyl sulphate (2 c.c.), when much heat is liberated, part of the base dissolves, and in a short time the methosulphate begins to separate and the whole soon becomes semi-solid. After heating in boiling water for a few minutes, the product is dissolved in boiling methyl alcohol, from which the methosulphate separates in glistening groups of needles which exhibit a beautiful lilac fluorescence.

Another convenient method of preparing the same substance is to mix finely powdered tetrahydromethylcryptopine (p. 897) with three times its weight of methyl sulphate, when it gradually dissolves and, on heating on the steam-bath, a reaction sets in with evolution of gas. After about half an hour, and before the liquid commences to darken, the product is mixed with two volumes of methyl alcohol and left in the ice-chest; the crystals are then collected and washed with methyl alcohol. The yield is about 70 per cent. of that theoretically possible:

0·3238 gave 0·1577 $BaSO_4$. S = 6·7.

$C_{22}H_{27}O_4N,Me_2SO_4$ requires S = 6·5 per cent.

Anhydrotetrahydromethylcryptopine methosulphate shrinks somewhat at 130° and melts at about 195—197° without decomposition to a colourless syrup. It is not very readily soluble in cold water, but dissolves easily on warming, and exhibits the characteristic property that the hot solution, on cooling, gelatinises, and does not crystallise until a crystal is introduced.

The addition of 50 per cent. potassium hydroxide to the aqueous solution gives no precipitate, but, on boiling, the odour of trimethylamine becomes at once apparent, the solution clouds, and an oil separates, which on cooling solidifies and doubtless consists of cryptopidene (see next page). The methosulphate is readily soluble

in glacial acetic acid, and gives, on the addition of sulphuric acid, a crimson solution, which almost immediately gives place to an intense port-wine colour.

In order to prepare *cryptopidene*, the finely powdered methosulphate (5 grams) was mixed with methyl-alcoholic potassium hydroxide (50 c.c. of 25 per cent.) in a flask fitted with a delivery tube dipping under dilute hydrochloric acid, and heated on the steam-bath for half an hour and subsequently in a salt-bath until nearly all the methyl alcohol had distilled over. The hydrochloric acid solution was evaporated to a small bulk and mixed with platinic chloride, when, on keeping, the characteristic orange prisms of trimethylamine platinichloride separated. (Found, Pt = 36·4. $(NMe_3)_2H_2PtCl_6$ requires Pt = 36·9 per cent.)

The residue in the flask was almost colourless, and yielded, on treatment with dilute hydrochloric acid, a somewhat viscid mass which, in contact with methyl alcohol, soon became quite hard. This substance is very sparingly soluble in methyl or ethyl alcohols, and separates from these solvents in two distinct forms, namely, either in small warty masses or in long, glistening, striated needles, and the latter appears to be the stable form, since it was noticed that the warty masses, when left in the mother liquor for some weeks, had changed completely into the glistening needles. Both modifications melt at approximately the same temperature, and the glistening needles do not become opaque on drying in the water-oven. In the following analyses (I) was carried out with the warty variety, (II) with the needle modification:

(I) 0·1104 gave 0·2980 CO_2 and 0·0622 H_2O. C = 73·6; H = 6·3.
(II) 0·1175 „ 0·3183 CO_2 „ 0·0658 H_2O. C = 73·9; H = 6·2.
$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

Cryptopidene melts at 124°, and is readily soluble in acetone, chloroform, ethyl acetate, or benzene, but sparingly so in light petroleum; it is appreciably soluble in ether, yielding a solution which has a lilac fluorescence. The solution of a trace of the substance in a drop of acetic acid gives, on the addition of sulphuric acid, an intense port-wine coloration. When the solution of cryptopidene in chloroform was titrated with a standard solution of bromine in chloroform, it readily absorbed 4 atoms of bromine, and, on allowing the solvent to evaporate by exposure to air, a brown, semi-solid mass resulted, which was not further examined.

Oxidation of Cryptopidene.—In investigating this oxidation cryptopidene (5 grams), dissolved in acetone (150 c.c.), was cooled to 0°, mixed with a solution of potassium hydroxide (0·3 gram) in acetone, and then finely-powdered permanganate added in small quantities at a time while the whole was vigorously stirred. Except

at the commencement, oxidation took place fairly rapidly until 12 grams had been added; the whole was then allowed to remain for twenty-four hours, filtered, and the manganese precipitate (*A*) well washed with acetone. The acetone extract was evaporated to dryness and the considerable syrupy residue distilled in a current of steam, when a colourless solid (0·27 gram) passed over, which melted at 72—73°, and consisted of 5:6-methylenedioxy-*o*-tolualdehyde, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$ (p. 907).

The residue in the steam-distillation flask was extracted with ether, the ethereal solution dried, evaporated, the brown residue dissolved in methyl alcohol and mixed with semicarbazide acetate, causing a crystalline substance immediately to separate, which melted at about 225° and consisted of the semicarbazone of 4:5-dimethoxy-2-vinylbenzaldehyde, $(MeO)_2C_6H_2(CHO){\cdot}CH{:}CH_2$ (p. 904). The manganese precipitate (*A*) was thoroughly extracted with hot water, the brown solution, while still hot, rendered just acid to Congo paper by adding dilute hydrochloric acid, when a small quantity of a somewhat viscid, ochreous substance (*B*) separated. This was collected, dissolved in dilute sodium carbonate, and, after boiling for an hour with animal charcoal, the acid was reprecipitated and crystallised from dilute acetic acid, when glistening plates resulted (0·6 gram), which melted at 213—215° and consisted of 5:6-methylenedioxy-*o*-toluic acid, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$ (p. 916). The brown filtrate from the ochreous precipitate (*B*) was concentrated to a small bulk by distillation under diminished pressure, mixed with more hydrochloric acid, and thoroughly extracted with ether on the machine; the ethereal solution was then evaporated, when a pale brown syrup (3 grams) remained, which had the odour of acetic acid and on keeping became semi-solid. This was dissolved in hot water, decolorised by animal charcoal, and allowed to remain in the ice-chest for a month, during which a crystalline crust (0·54 gram) separated, which melted at 175—180° and was nearly pure *m*-opianic acid,

$$(MeO)_2C_6H_2(CHO){\cdot}CO_2H$$

(see below). The filtrate from this acid was made alkaline with ammonia and boiled with barium chloride, the insoluble barium salt was collected, washed, and dissolved in hot dilute hydrochloric acid, when a considerable crust of *m*-hemipinic acid crystallised on cooling.

4:5-*Dimethoxy-2-aldehydobenzoic Acid* (m-*Opianic Acid*), $(MeO)_2C_6H_2(CHO){\cdot}CO_2H$.

The formation of this important acid by the oxidation of cryptopidene with permanganate was described in the previous Section. It

is readily purified by recrystallisation from water, in which it is sparingly soluble in the cold and from which it separates as a sandy powder resembling fumaric acid, or as a mass of colourless needles, according to the concentration and rate of cooling. It melts at 183—184°, is immediately soluble in cold sodium carbonate, and reprecipitated on the addition of hydrochloric acid:

0·1365 gave 0·2861 CO_2 and 0·0605 H_2O. C = 57·0; H = 4·9.
$C_{10}H_{10}O_5$ requires C = 57·1; H = 4·8 per cent.

Titration: 0·1212 required for neutralisation 5·9 c.c. *N*/10-NaOH, whereas this amount of a monobasic acid, $C_{10}H_{10}O_5$, should neutralise 5·8 c.c.

The *oxime*, $(MeO)_2C_6H_2(CO_2H)\cdot CH{:}N\cdot OH$, is readily produced when *m*-opianic acid (0·5 gram), dissolved in excess of potassium hydroxide, is mixed with hydroxylamine hydrochloride (0·5 gram). The solution was allowed to remain for twenty-four hours and acidified with hydrochloric acid, which caused a voluminous, gelatinous precipitate to separate, and this was extracted with much ether. On concentrating the carefully dried ethereal solution to a small bulk, the oxime separated as a chalky, crystalline precipitate, and was collected, washed with ether, and dried in a desiccator:

0·1113 gave 0·2174 CO_2 and 0·0506 H_2O. C = 53·3; H = 5·0.
0·2255 „ 12·3 c.c. N_2 at 18° and 764 mm. N = 6·3.
$C_{10}H_{11}O_5N$ requires C = 53·3; H = 4·9; N = 6·2 per cent.

m-*Opianic acid oxime* has no definite melting point, but when rapidly heated in a capillary tube it decomposes vigorously at about 140° and the pale yellow syrup soon solidifies to a mass which does not melt at 250° and doubtless consists of *m*-hemipinimide (see p. 930). It is sparingly soluble in cold water, but dissolves on boiling, and the solution deposits a crystalline mass, which appears to consist of the anhydride; the oxime is also readily soluble in cold dilute sodium carbonate.

m-*Opianic Acid Oxime Anhydride*, $(MeO)_2C_6H_2\begin{matrix}CO-O\\ CH{:}N\end{matrix}$.—This substance is obtained when *m*-opianic acid (0·5 gram) is mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (0·4 gram) and then absolute alcohol (5 c.c.) added. On continuously stirring, the crystals of the acid, whilst not passing into solution, rapidly change in appearance, and in a short time the whole sets to a paste of the oxime anhydride. The satiny, crystalline mass was collected, thoroughly washed with water, in which it is sparingly soluble, drained on porous porcelain, and dried at 50—60°:

0·1027 gave 0·2174 CO_2 and 0·0418 H_2O. C = 57·7; H = 4·5.
0·1601 ,, 9·0 c.c. N_2 at 15° and 760 mm. N = 6·6.
$C_{10}H_9O_4N$ requires C = 57·9; H = 4·3; N = 6·8 per cent.

This oxime-anhydride decomposes at about 132—135°, with a slight puff, to a pale yellow syrup, which immediately solidifies, becomes colourless, and does not melt at 250°. The substance produced in this way is m-*hemipinimide*, $(MeO)_2C_6H_2<^{CO}_{CO}>NH$, isomeric change taking place of a similar kind to that involved in the formation of hemipinimide by the action of heat on the oximes of opianic or ψ-opianic acids (compare p. 827). When the heating was carried out with 0·5 gram of the substance it seemed as if the change was not accompanied by the liberation of so much heat as in the other cases mentioned. The product was almost insoluble in all the usual organic solvents, but separated from boiling acetophenone in pearly groups of fern-like needles, and, after washing with acetone and then methyl alcohol, the following analytical results were obtained:

0·2303 gave 13·5 c.c. N_2 at 17° and 762 mm. N = 6·8.
$C_{10}H_9O_4N$ requires N = 6·8 per cent.

m-*Hemipinimide* does not appear to have been described, and, in order to obtain it for the sake of comparison, *m*-hemipinic acid was dissolved in excess of dilute ammonia, the solution evaporated, and the dry salt heated in a test-tube with a free flame until decomposition was complete and the fused mass no longer effervesced. During this operation a considerable sublimate was produced and, on recrystallising the whole from acetophenone, the crystals exactly resembled those obtained by the action of heat on *m*-opianic acid oxime anhydride and did not melt at 300°.

m-*Opianic Acid Semicarbazone*,
$(MeO)_2C_6H_2(CO_2H)\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$.

The addition of semicarbazide acetate to the solution of *m*-opianic acid in boiling water causes the separation of the semicarbazone as an apparently gelatinous precipitate, which, however, under the microscope is seen to consist of a voluminous mass of felted needles:

0·2252 gave 31·1 c.c. N_2 at 18° and 750 mm. N = 15·5.
$C_{11}H_{13}O_5N_3$ requires N = 15·7 per cent.

This semicarbazone decomposes at about 227° with vigorous evolution of gas; it is very sparingly soluble in water, but dissolves immediately in cold dilute sodium carbonate.

Acetyl-m-*opianic Acid*, $(MeO)_2C_6H_2<^{CH(OAc)}_{CO-\!\!-}>O$.—In order to

prepare this characteristic derivative, the acid (1 gram), dissolved in hot, freshly distilled, acetic anhydride (10 c.c.), was heated to boiling for fifteen minutes and the bulk of the acetic anhydride distilled off, when the residue rapidly crystallised. After collecting and washing with acetic anhydride, the substance melted at 155—156°, and recrystallisation from the same solvent raised the melting point to 158—159°:

0·1105 gave 0·2305 CO_2 and 0·0488 H_2O. C=56·9; H=4·9.

$C_{12}H_{12}O_6$ requires C=57·1; H=4·8 per cent.

Acetyl-m-*opianic acid* dissolves appreciably in boiling water, and separates unchanged if the solution is rapidly cooled; it is insoluble in cold dilute sodium carbonate, but dissolves readily on boiling.

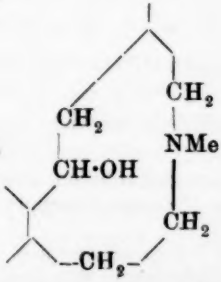
When 0·1600 gram of the acetyl acid was boiled with excess of *N*/10-NaOH and titrated back, it was found that 13·0 c.c. had been neutralised, whereas this amount of a substance, $C_{12}H_{12}O_6$, becoming dibasic, requires 12·7 c.c. for neutralisation. That hydrolysis had taken place was shown by the fact that the solution deposited, on acidifying, pure *m*-opianic acid melting at 183—184°.

Reduction of m-*Opianic Acid to* m-*Meconine*, $(MeO)_2C_6H_2\langle\begin{matrix}CH_2\\CO\end{matrix}\rangle O$.

m-Opianic acid is readily reduced when its solution in sodium carbonate is treated with excess of sodium amalgam, first at the ordinary temperature and then on the steam-bath. The addition of hydrochloric acid to the product yielded a clear solution which, on vigorously stirring, rapidly deposited crystals, and these, after recrystallising from very dilute alcohol, melted at 155—157° and consisted of m-*meconine*.

Section VI.

Dihydrocryptopine, $C_{21}H_{25}O_5N$,



Unlike berberine, cryptopine does not appear to be reduced even at the boiling temperature when the solutions in acids are treated with zinc or tin, but it is reduced with the addition of two atoms of hydrogen when the solution of the sulphate in dilute sulphuric

acid is boiled with sodium amalgam, although the process does not seem to proceed to completion. Cryptopine (3 grams) is dissolved in hot water (300 c.c.) and sulphuric acid (5 c.c.) in a porcelain basin, the solution allowed to cool to 50°, and then sodium amalgam (250 grams of 4 per cent.) added all at once. When the vigorous reaction is over, the whole is heated to boiling with the addition, from time to time, of small quantities of dilute sulphuric acid until the sodium amalgam is completely decomposed. After filtering, the acid solution is mixed with excess of 40 per cent. sodium hydroxide, when a gelatinous precipitate separates which, in this condition, is readily soluble in ether.

The whole is therefore repeatedly extracted with considerable quantities of ether,* the ethereal solution dried over potassium carbonate, and immediately filtered; otherwise the dihydrocryptopine will crystallise on the potassium carbonate. The ethereal solution is then concentrated considerably, during which, and particularly on subsequently keeping in the ice-chest, a crystalline crust separates. When this is collected and dried it melts at 181—183° and looks like a pure substance, but it always contains unchanged cryptopine, and sometimes in considerable quantities. In order to remove this, the whole is dissolved in a boiling dilute solution of oxalic acid (3 grams), the solution of the mixed oxalates concentrated considerably, and allowed to cool very slowly (otherwise a gelatinous mass separates), when, at the right concentration, cryptopine hydrogen oxalate separates readily and almost completely in groups of glistening needles. The filtrate from this salt yields, on further concentration, the much more readily soluble salt of dihydrocryptopine in long, thin needles, and this may be separated and purified by recrystallisation. The usual procedure, however, was to add excess of sodium hydroxide to the filtrate from the cryptopine oxalate and crystallise the bulky precipitate of dihydrocryptopine from ether or methyl alcohol †:

0·1307 gave 0·3245 CO_2 and 0·0808 H_2O. C = 67·7; H = 6·9.
0·4761 „ 15·6 c.c. N_2 at 16° and 757. N = 3·8.
$C_{21}H_{25}O_5N$ requires C = 67·9; H = 6·7; N = 3·7 per cent.

* The aqueous solution, after the ether extraction, contains the α- and β-chlorides of *iso*dihydrocryptopine and the isolation of these is described on p. 934.

† When dihydrocryptopine is precipitated from its salts with organic acids, and apparently also from its salts with mineral acids, by the addition of ammonia, it separates as a chalky mass which, after collecting, washing and drying over phosphoric oxide, shrinks and nearly melts at 85°, effervesces at 105°, becomes solid again and then melts at 185°. In this condition it appears to contain one molecule of water, since it yielded, on analysis, C = 65·1; H = 7·0, whereas $C_{21}H_{25}O_5N,H_2O$ requires C = 65·4; H = 7·0 per cent.

Dihydrocryptopine melts at 187—188°, and is readily soluble in hot alcohol, benzene, ethyl acetate, or acetone, but sparingly so in ether or light petroleum; it crystallises well from methyl alcohol in crusts of prisms. The solution of a trace of the substance in a drop of acetic acid gives, on the addition of sulphuric acid, an intense port-wine coloration. The salts of dihydrocryptopine are much more readily soluble than those of cryptopine, and crystallise well.

The *platinichloride* separates on the addition of platinic chloride to the dilute solution of the hydrochloride as a gelatinous mass which, on warming, becomes crystalline:

0·1306 gave 0·2107 CO_2 and 0·0518 H_2O. C=44·0; H=4·4.
0·3854 „ 0·0663 Pt. Pt=17·2.
$(C_{21}H_{25}O_5N)_2H_2PtCl_6$ requires C=43·7; H=4·4;
Pt=17·0 per cent.

The solution of dihydrocryptopine hydrochloride gives with mercuric chloride a colourless jelly which, on heating, dissolves and then crystallises as a very sparingly soluble, sandy powder consisting of microscopic prisms. The picrate is a chrome, amorphous precipitate, somewhat soluble in boiling water.

The Quaternary Salts of iso*Dihydrocryptopine.*

In discussing the conversion of dihydrocryptopine into the salts of *iso*dihydrocryptopine it was pointed out (p. 839) that whereas only one chloride of *iso*cryptopine has so far been prepared, two well characterised (α- and β-) *iso*dihydrocryptopine chlorides have been isolated and carefully examined. Of these, the much less readily soluble β-salt is the more easily obtained, and has been prepared in considerable quantities by one or other of the following processes:

(I) Dihydrocryptopine (5 grams) is mixed with acetyl chloride (10 c.c.) and heated in a reflux apparatus just to boiling, when the base gradually and completely dissolves and, after a time, a white salt commences to separate. The heating is continued for about half an hour, the excess of acetyl chloride removed by distillation from the water-bath, when a porous, chalky, crystalline cake remains which is sparingly soluble in hot water and crystallises as a voluminous mass of groups of slender needles which fill the whole solution. This substance is *iso*dihydrocryptopine β-chloride, and is collected, washed with dilute hydrochloric acid, and drained on porous porcelain, when it dries to a curious and characteristic opaque, horny mass.*

* The filtrate contains *iso*dihydrocryptopine α-chloride (compare p. 934.)

(II) Dihydrocryptopine (5 grams) is digested on the water-bath with phosphoryl chloride (20 c.c.), when solution rapidly takes place with the evolution of hydrogen chloride and a salt, presumably the hydrochloride, separates, but this again passes into solution. After three hours, the excess of phosphoryl chloride is distilled off from the water-bath under diminished pressure, and the residue crystallised from water as before *:

0·1027 gave 0·2413 CO_2 and 0·0588 H_2O. C = 64·2; H = 6·4.
0·2596 „ 0·0931 AgCl. Cl = 8·9.
$C_{21}H_{24}O_4NCl$ requires C = 64·7; H = 6·2; Cl = 9·1 per cent.

iso*Dihydrocryptopine β-chloride* begins to darken at about 210°, is brick-red at 230°, but does not melt at 260°. It is decomposed with difficulty by alkalis, and even when heated with 25 per cent. aqueous potassium hydroxide for several minutes much of the chloride remains. It is, however, gradually decomposed by boiling with methyl-alcoholic potassium hydroxide, and this change is described on p. 941.

The *β-platinichloride* is obtained on the addition of platinic chloride to the hot solution of the β-chloride in dilute hydrochloric acid as a pale ochreous, chalky precipitate which is almost insoluble in water or boiling alcohol. It darkens somewhat at 240°, and decomposes at about 250—253°, with frothing, to a black mass:

0·2689 gave 0·0469 Pt. Pt = 17·4.
$(C_{21}H_{24}O_4N)_2PtCl_6$ requires Pt = 17·4 per cent.

iso*Dihydrocryptopine β-Iodide*.—This salt is obtained as a voluminous, gelatinous precipitate when potassium iodide is added to a hot solution of the β-chloride. On warming on the steam-bath the gelatinous mass becomes quite granular and very sparingly soluble, and the precipitate under the microscope is seen to consist of leafy masses. The substance was collected and drained on porous porcelain in the dark, since light causes it gradually to become brown. After drying at 100° the salt did not melt at 250°:

0·1164 gave 0·2255 CO_2 and 0·0559 H_2O. C = 52·8; H = 5·3.
0·3729 „ 9 c.c. N_2 at 17° and 758 mm. N = 2·8.
$C_{21}H_{24}O_4NI$ requires C = 52·4; H = 5·0; N = 2·9 per cent.

iso*Dihydrocryptopine α-Chloride*.—Considerable quantities of this chloride were obtained during the examination of the mother liquors from the preparation of dihydrocryptopine (p. 932). In this preparation the yield of base obtained when sodium hydroxide is added to the acid solution of the product of the reduction is not more than 60—70 per cent. of that theoretically possible. In order

* The filtrate contains isodihydrocryptopine α-chloride.

to discover the reason for this, the alkaline solution was rendered acid by the addition of a large excess of hydrochloric acid, when a small amount of a gelatinous precipitate separated which proved to be the β-chloride. The filtrate yielded, on the addition of excess of mercuric chloride, a heavy precipitate, which was collected, washed thoroughly, suspended in water, and decomposed by hydrogen sulphide, when the filtrate, on keeping, gave a further small, gelatinous precipitate of the β-chloride. On concentrating the mother liquor to a small bulk by distilling off the water under diminished pressure and then allowing to cool slowly, stout, prismatic needles separated, mixed with slender needles, and the latter, which proved to consist of the β-chloride, could be mechanically separated by shaking and decanting. After several recrystallisations, and each time mechanically separating the small quantity of the β-chloride which separated, the prismatic crystals were obtained quite pure, and examination showed that these consisted of *iso*dihydrocryptopine α-chloride. In an exactly similar manner considerable quantities of the α-chloride were obtained from the mother liquors of the preparation of the β-chloride (p. 933). The air-dry salt appears to contain $4H_2O$, which is slowly removed at 100°, but not without slight decomposition:

0·1295 gave 0·2620 CO_2 and 0·0807 H_2O. C = 55·2; H = 6·9.
0·7848, dried at 100—105° until constant, lost 0·1185. H_2O = 15·1.

$C_{21}H_{24}O_4NCl,4H_2O$ requires C = 54·8; H = 6·9; H_2O = 15·6 per cent.

The dry salt yielded C = 64·2; H = 6·2; Cl = 8·9, whereas $C_{21}H_{24}O_4NCl$ requires C = 64·6; H = 6·2; Cl = 9·1 per cent.

iso*Dihydrocryptopine α-chloride* is very different from the β-chloride in its properties. The anhydrous salt softens at 145°, melts almost completely with effervescence at 165°, then becomes solid again, gradually darkens, is brown at 200°, and froths up at 230° to a brown mass.

The air-dried hydrated salt softens at 80—85°, melts partly at 95°, and then becomes solid again. Unlike the β-chloride, it is very readily soluble in water and crystallises splendidly, and the addition of hydrochloric acid does not appear materially to affect the solubility.

The aqueous solution of the α-chloride gives no precipitate on the addition of ammonia, but it is apparently more readily decomposed by potassium hydroxide than the β-chloride, and its behaviour with methyl-alcoholic potassium hydroxide is described on p. 937. The addition of mercuric chloride to the dilute solution of the α-chloride produces a chalky precipitate, which is comparatively readily

soluble in hot water and crystallises well as a crust which, under the microscope, is seen to consist of long prisms with bevelled edges.

Mr. Barker has kindly measured the crystals of the α-chloride and finds the substance to be anorthic. As will be seen from Fig. 4, the form consists of a prismatic zone of three faces,

FIG. 4

iso*Dihydrocryptopine α-chloride.*

b, *m*, *n*, terminated obliquely by the face *c*. The face *b* is always striated vertically. The following mean measurements were obtained:—

Face	ϕ.	ρ.
b	0°	90°
m	$<9\frac{1}{2}$	90
n	109	90
c	76	50

It is impossible to calculate a complete set of crystallographic constants owing to the paucity of angles. Optically, the extinction is oblique on all the faces.

The α-Platinichloride.—This salt, prepared in the usual manner by adding platinic chloride to the hot solution of the α-chloride in very dilute hydrochloric acid, is a pale yellow, sparingly soluble, crystalline precipitate. It scarcely darkens below 200°, shrinks and begins to effervesce at 210°, and decomposes vigorously at 215° to a voluminous, red mass:

0·1155 gave 0·1885 CO_2 and 0·0453 H_2O. C = 44·5; H = 4·3.

0·2493 „ 0·0435 Pt. Pt = 17·4.

$(C_{21}H_{24}O_4N)_2PtCl_6$ requires C = 45·1; H = 4·3; Pt = 17·4 per cent.

iso*Dihydrocryptopine α-Iodide.*—The addition of potassium iodide to the moderately concentrated solution of the α-chloride gives a milky solution, and a gummy salt separates which gradually crystal-

lises. If, however, potassium iodide is added to the very weak solution the milkiness first produced dissolves again, and, on warming, the iodide separates beautifully in groups of four-sided prisms with truncated corners. This salt is almost insoluble in cold water and only very sparingly so in hot water; it darkens slightly at 225—230°, and then the substance, in the upper part of the tube and in contact with air, becomes deep reddish-brown whilst the remainder is ochreous; at 275—280° it decomposes with effervescence to a brown mass:

0·1101 gave 0·2092 CO_2 and 0·0535 H_2O. C=51·8; H=5·3.

$C_{21}H_{24}O_4NI$ requires C=52·4; H=5·0 per cent.

iso*Dihydrocryptopine α-Bromide*.—This fine salt was obtained as the result of an experiment made with the object of determining whether magnesium ethyl bromide has any action on the α-chloride. The finely powdered α-chloride (1 gram) was added to an ethereal solution of magnesium ethyl bromide, containing 0·3 gram of magnesium, and the whole heated for twenty-four hours on the steam-bath; the ether was then evaporated and the pasty residue rubbed with a slight excess of dilute hydrochloric acid. The granular precipitate was collected and separated from boiling water, in which it is less readily soluble than the α-chloride, in clustres of needles which become opaque in the steam-oven, darken somewhat at 235°, but do not melt at 270°:

0·1049 gave 0·2223 CO_2 and 0·0537 H_2O. C=57·8; H=5·7.

0·1818 „ 0·0786 AgBr. Br=18·4.

$C_{21}H_{24}O_4NBr$ requires C=58·1; H=5·5; Br=18·4 per cent.

When this salt was digested with methyl-alcoholic potassium hydroxide it was readily decomposed with the formation of a mixture of the *A*- and *B*-modifications of anhydrodihydrocryptopine (next section).

The A- *and* B-*Modifications of Anhydrodihydrocryptopine*, $C_{21}H_{23}O_4N$. (Formulæ, p. 841.)

These substances are produced when either the α- or β-modifications of *iso*dihydrocryptopine chloride are digested with methyl-alcoholic potassium hydroxide under the conditions described below (I and II),

$$C_{21}H_{24}O_4NCl = C_{21}H_{23}O_4N + HCl,$$

or treated with silver hydroxide and the carbinol base dehydrated by evaporation to dryness under diminished pressure (III and IV):

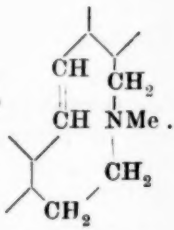
$$C_{21}H_{24}O_4N\cdot OH = C_{21}H_{23}O_4N + H_2O.$$

(I) α-*iso*Dihydrocryptopine chloride (4 grams) was finely ground, sifted, mixed with methyl-alcoholic potassium hydroxide (10 c.c. of 25 per cent.), and boiled for ten minutes, when decomposition took

place readily, potassium chloride separated, and, on the addition of water to the milky syrup, a caseous precipitate was produced which, on shaking, soon became hard and crystalline. This was collected, washed thoroughly, drained on porous porcelain, and dissolved in hot acetone; the filtered solution was then concentrated considerably and left for a few days in the ice-chest, when a crust separated which melted at 172—175° and consisted of nearly pure *A*, anhydrodihydrocryptopine (see below). The mother liquor was allowed to evaporate considerably and again left in the ice-chest, when the concentrated solution deposited four-sided plates, like sugar crystals, and these, after washing with methyl alcohol, melted at 125—126° and consisted of *B* (p. 941).

(II) By far the larger amounts of the bases *A* and *B*, used in the investigations described in the following pages, were prepared from the more readily accessible horny *iso*dihydrocryptopine β-chloride. This salt appears to be decomposed by alkali with considerably more difficulty than the α-chloride, and it was necessary to digest it (8 grams) with a large excess of methyl-alcoholic potassium hydroxide (25 c.c. of 25 per cent.) for an hour,* and even then elimination of hydrogen chloride was not quite complete. On adding water to the resulting syrup a caseous mass was again precipitated, and this was collected, washed, dried, extracted with acetone, filtered from a little unchanged chloride, and the acetone extract treated as described under (I), when the product was found to consist mainly (3 grams) of *A*, and the mother liquor on evaporating and digesting with methyl alcohol yielded 1 gram of *B*. A further quantity of the latter substance was obtained by evaporating the methyl-alcoholic mother liquors to dryness, adding hydrochloric acid, recrystallising the sparingly soluble hydrochloride (p. 943), and decomposing it with sodium hydroxide.

Anhydrodihydrocryptopine (*A*), $C_{21}H_{23}O_4N$,



This base is generally less soluble in the usual solvents than *B* (p. 941); it is particularly sparingly soluble in methyl alcohol and also sparingly so in alcohol, acetone, or benzene in the cold, but much more readily so on boiling, and crystallises well from all

* Care must be taken to avoid local overheating, otherwise decomposition takes place with the formation of a deep purple solid.

these solvents, from alcohol in balls of needles, from acetone in four-sided prisms, and from benzene as a crust of microscopic prisms:

0·1343 gave 0·3513 CO_2 and 0·0789 H_2O. C = 71·3; H = 6·5.
0·3978 „ 13·8 c.c. N_2 at 16° and 760 mm. N = 4·0.
$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5; N = 4·0 per cent.

Anhydrodihydrocryptopine (*A*) melts at 178°, and a fragment of a crystal dissolved in a drop of acetic acid gives, on the addition of sulphuric acid, an intense reddish-brown solution which, on long keeping, becomes bluish-violet. When it is boiled with alcohol in a reflux apparatus, it is gradually converted into *B* (see p. 941), and therefore unless the operation is rapidly carried out and with only small quantities, it is inadvisable to crystallise the base from this solvent.

Salts of Anhydrodihydrocryptopine (*A*).—The most important characteristic of these salts is that they are much more readily soluble than the corresponding salts of *B* and crystallise with much less facility. They dissolve more freely in water than in solutions of dilute acids.

The Hydrochloride.—Base *A* dissolves quite readily in dilute hydrochloric acid and, on keeping, the concentrated solution deposits a crystalline powder consisting of microscopic balls of needles. When rapidly heated in a capillary tube the salt gradually becomes discoloured, is ochreous at 200°, reddish-brown at 230°, but does not melt at 250°.

The *sulphate* is also readily soluble, and separates in indistinct, warty masses from the rather concentrated solution in excess of acid.

The *hydriodide* is obtained, on the addition of potassium iodide to the hydrochloride, as a caseous precipitate, which dissolves in boiling water and crystallises on rubbing in warty masses. The *platinichloride* separates on adding platinic chloride to the warm solution of the hydrochloride as a pale ochreous, caseous precipitate which soon becomes crystalline and is somewhat soluble in hot water. It darkens at 200° and decomposes completely at 215—220° to a reddish-brown mass:

0·2025 gave 0·0350 Pt. Pt = 17·3.
$(C_{21}H_{23}O_4N)_2,H_2PtCl_6$ requires Pt = 17·4 per cent.

Conversion of Base (*A*) *into the β-Chloride of* iso*Dihydrocryptopine.*

This change was brought about by evaporating the solution of the hydrochloride in a large excess of dilute hydrochloric acid on

the water-bath, adding more hydrochloric acid, and repeating the evaporation several times. The resulting concentrated solution deposited a voluminous mass of crystals which, on examination, proved to consist mainly of *iso*dihydrocryptopine β-chloride.

Anhydrodihydrocryptopine (*A*) *Methosulphate*, $C_{21}H_{23}O_4N,Me_2SO_4$.

In preparing this derivative 2 grams of the base *A* dissolved in hot benzene (12 c.c.) and cooled to 40° are rapidly mixed with methyl sulphate (2 c.c.), when there is some rise of temperature and a gum separates.

After remaining, sometimes for several hours, the gum gradually develops warty groups, and when the whole is now stirred, crystallisation rapidly proceeds throughout the mass, the benzene may then be decanted and the crystalline methosulphate collected and washed with benzene. After remaining in contact with porous porcelain, the substance is readily obtained pure by two crystallisations from methyl alcohol, in which it is rather sparingly soluble in the cold, and from which it separates as a voluminous mass of microscopic, flat needles:

0·2301 gave 0·1170 $BaSO_4$. S = 6·9.

$C_{21}H_{23}O_4N,Me_2SO_4$ requires S = 7·0.

When rapidly heated *anhydrodihydrocryptopine* (*A*) *methosulphate* shrinks to about 190°, and melts suddenly, without effervescence, at about 240—242° to a yellow syrup, which soon becomes orange-red. It is very readily soluble in water, and separates from the concentrated solution in warty masses; the aqueous solution gives, on the addition of concentrated aqueous potassium hydroxide, a precipitate of the undecomposed methosulphate, but when the whole is boiled an oil separates which is insoluble in water, crystallises on cooling, and evidently consists of methyl*iso*anhydrodihydrocryptopine (p. 945).

The Methiodide, $C_{21}H_{23}O_4N,MeI$.—The addition of potassium iodide to the solution of the methosulphate in hot water produces a milky liquid, from which a viscid precipitate separates. When the solution is boiled, the precipitate melts, then suddenly begins to crystallise, and the decanted supernatant liquid deposits the pure methiodide as a crystalline mass which, under the microscope, is seen to consist of groups of well-developed prisms:

0·1114 gave 0·2180 CO_2 and 0·0505 H_2O. C = 53·3; H = 5·0.

$C_{22}H_{26}O_4NI$ requires C = 53·4; H = 5·1 per cent.

This *methiodide* remains colourless below 220°, is yellow at 225°, shrinks at 230°, and melts at about 235—240° to an amber gum. It is appreciably soluble in alcohol, and may be recrystallised from

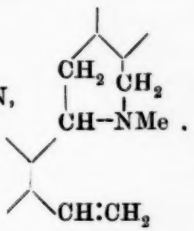
this solvent, but apparently with slight decomposition, since the crystals are yellow and melt at about 225°. The *methochloride*, $C_{21}H_{23}O_4N$,MeCl, was prepared by digesting the iodide with silver chloride and water on the steam-bath and concentrating the filtered liquid, when it separated in rather indefinite, pasty crusts:

0·2395 gave 0·0885 AgCl. Cl = 9·0.

$C_{22}H_{26}O_4NCl$ requires Cl = 8·8 per cent.

This substance decomposes at 215—220° with effervescence and formation of a yellow froth, is very soluble in water, and appears to be decomposed even by very concentrated potassium hydroxide only with difficulty. It gives a deep crimson colour when its solution in acetic acid is mixed with sulphuric acid.

Anhydrodihydrocryptopine (*B*), $C_{21}H_{23}O_4N$,



It has already been stated (p. 850) that this substance is produced when anhydrocryptopine is reduced in sulphuric acid solution with sodium amalgam; it is also formed when anhydrodihydrocryptopine, *A* (m. p. 178°), is boiled with alcohol until solution is complete, and then for a further hour when, on concentrating, the solution deposits a colourless, crystalline crust melting at 125—127° and consisting of Base *B*. Most of the Base *A*, used in the following experiments, was, however, prepared from the horny *iso*dihydrocryptopine *β*-chloride by the action of methyl-alcoholic potassium hydroxide (compare p. 934).

It was usually purified by recrystallisation from methyl alcohol, in which it is moderately readily soluble and from which it separates in brilliant prisms; these, as usually prepared, are pale amber, but the substance, obtained, for example, from the recrystallised, colourless hydrochloride, is in reality colourless:

0·1047 gave 0·2737 CO_2 and 0·0616 H_2O. C = 71·3; H = 6·5.

0·4228 „ 14·8 c.c. N_2 at 17° and 756 mm. N = 4·1.

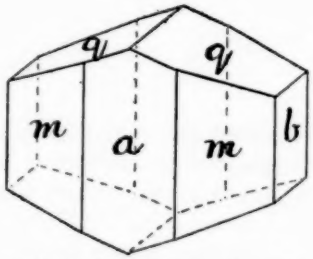
$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·8; N = 4·0 per cent.

Anhydrodihydrocryptopine (*B*) melts at 126—127°, and is readily soluble in alcohol, benzene, acetone, ethyl acetate, or chloroform, but sparingly so in light petroleum. A trace of the substance dissolved in a drop of acetic acid gives with sulphuric acid a yellowish-brown solution, which deepens on keeping and becomes

purple. Unlike Base *A*, it is not changed by boiling with methyl alcohol, since, after two hours, the concentrated solution deposited lemon-yellow crusts which melted at 125—126°. It also does not appear to be affected by boiling with acetic anhydride. An attempt was made to reduce it by boiling the solution in dilute sulphuric acid with a large excess of sodium amalgam, but the caseous precipitate which separated on the addition of potassium hydroxide crystallised from methyl alcohol in transparent, colourless prisms which melted at 126° and consisted of the unchanged base. The crystals obtained from methyl alcohol were measured by Miss M. W. Porter, who finds the system to be monoclinic with the axial ratios $a:b:c=0{\cdot}3752:1:0{\cdot}3427$; $\beta=96°0'$.

The observed forms were: $b\{010\}$, $a\{100\}$, $q\{011\}$, and $m\{110\}$. The crystals were of a stout, prismatic habit, and doubly terminated, as is shown in Fig. 5, the form $q\{011\}$ being usually striated

FIG. 5.



Anhydrodihydrocryptopine (*B*).

parallel to the *a*-axis. There is a perfect cleavage parallel to $b\{010\}$. Optically the extinction on the latter face is 9° inclined to the edge *bm*. The results obtained from a measurement of five crystals are given in the following table:

Table of Measured and Calculated Angles.

		ϕ.			ρ.		
Face.	No.	Limits.	Mean.	Calc.	Limits.	Mean.	Calc.
b (010)	7	359°45′— 0°10′	0°0′	0°0′	89°56′—90°0′	90°0′	90°0′
a (100)	9	89 53 — 90 10	89 59	90 0	89 57 —90 4	90 1	90 0
m (110)	15	69 24 — 69 43	*69 32	—	89 52 —90 9	90 1	90 0
q (011)	6	16 32 — 17 33	*17 4	—	19 10 —20 23	*19 43	—

Fedorov Complex-symbol: $4d\,;\,5$ / 70 / $+3\frac{1}{2}$ Determinants: $\begin{Bmatrix}\bar{1}01\\101\\010\end{Bmatrix}$

Salts of Anhydrodihydrocryptopine (*B*).—The most striking difference between the Bases *A* and *B* is that, whereas the salts of

the former are readily soluble, those of *B* are sparingly soluble, and especially so in dilute acids, and are characterised by the ease with which they crystallise.

The Hydrochloride.—When brought into contact with dilute hydrochloric acid, Base *B* is converted at once into a solid cake of the hydrochloride, and this dissolves in much water and separates, on cooling, as a voluminous mass of slender needles which, when dry, have a brilliant, satiny appearance. The addition of hydrochloric acid even to very dilute aqueous solutions causes the salt to separate in micro-crystals:

0·2155 gave 0·0786 AgCl. Cl = 9·0.

$C_{21}H_{23}O_4N,HCl$ requires Cl = 9·1 per cent.

When heated in a capillary tube this hydrochloride remains colourless up to 200° and decomposes at 225° with vigorous effervescence to a yellow syrup.

The Sulphate.—Base *B* dissolves readily in hot dilute sulphuric acid, but almost immediately the very sparingly soluble sulphate commences to separate from the hot liquid in brilliant, mostly four-sided plates, and, although so sparingly soluble, this salt appears to be more readily so than the hydrochloride. The *hydriodide* is obtained as a caseous precipitate, which immediately becomes crystalline, when potassium iodide is added to the hot solution of the hydrochloride. It is very sparingly soluble in water. The *platinichloride* separates, on the addition of platinic chloride to the hot solution of the hydrochloride, as an ochreous, amorphous precipitate, which soon becomes crystalline:

0·2053 gave 0·0353 Pt. Pt = 17·2.

$(C_{21}H_{23}O_4N)_2H_2PtCl_6$ requires Pt = 17·4 per cent.

This double salt scarcely changes below 200°, and melts at about 223° to a dark brown mass.

Anhydrodihydrocryptopine (*B*) *Methosulphate*, $C_{21}H_{23}O_4N,MeSO_4$.

In the preparation of this substance, anhydrodihydrocryptopine (*B*, 5 grams), dissolved in just sufficient boiling benzene, is cooled to room temperature and the supersaturated solution immediately mixed with methyl sulphate (5 c.c.), when the methosulphate commences to separate at once and the whole becomes semi-solid. After some hours the mass is collected, washed thoroughly with benzene, dried on porous porcelain, and then crystallised from methyl alcohol, and finally from water, in which it is unusually sparingly soluble and from which it separates in four-sided plates which are generally lemon-yellow:

0·1178 gave 0·2483 CO_2 and 0·0643 H_2O. C = 57·5; H = 6·0.
0·2324 „ 0·1190 $BaSO_4$. S = 7·0.
$C_{21}H_{23}O_4N,Me_2SO_4$ requires C = 57·6; H = 6·0; S = 6·7 per cent.

Anhydrodihydrocryptopine (B) *methosulphate* decomposes, when rapidly heated, at about 245° with evolution of gas and formation of a deep orange-brown syrup. A trace, moistened with acetic acid and mixed with sulphuric acid, gives a fine pink colour like permanganate, and this gradually becomes port-wine colour. The methosulphate is readily reduced when its solution in dilute sulphuric acid is treated with a large excess of sodium amalgam and, on the addition of alkali, a syrupy base separates which dissolves in ether and is obtained, on evaporating the solvent, as a colourless gum. This base has not been further investigated.

Anhydrodihydrocryptopine (*B*) *Methiodide*, $C_{21}H_{23}O_4N,MeI$.—This salt is readily prepared by adding potassium iodide to the solution of the methosulphate, when a milky liquid is produced which soon crystallises. After collecting, the granular mass was dried in the steam-oven and analysed:

0·1129 gave 0·2212 CO_2 and 0·0551 H_2O. C = 53·4; H = 5·4.
$C_{22}H_{26}O_4NI$ requires C = 53·5; H = 5·3 per cent.

This *methiodide* does not discolour below 200°, is slightly ochreous at 230°, and melts sharply at 238° to an orange-red syrup which effervesces a few degrees higher. It dissolves with difficulty in boiling water, and separates on cooling as a granular, crystalline mass; it is also sparingly soluble in boiling alcohol, and the concentrated solution deposits the substance in microscopic, four-sided, flat plates with bevelled edges.

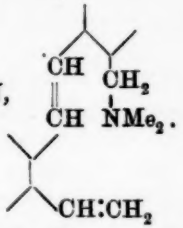
The *methochloride*, $C_{21}H_{23}O_4N,MeCl$, was prepared by boiling the finely divided iodide with much water and excess of silver chloride; the solution was concentrated considerably, and then left over sulphuric acid, when pale yellow, crystalline crusts gradually formed:

0·1224 gave 0·2917 CO_2 and 0·0715 H_2O. C = 65·0; H = 6·5.
0·2386 „ 0·0861 AgCl. Cl = 8·9.
$C_{22}H_{26}O_4NCl$ requires C = 65·4; H = 6·4; Cl = 8·8 per cent.

Anhydrodihydrocryptopine (*B*) *methochloride* softens at 230° and melts and decomposes with vigorous effervescence at about 240° to an orange-red froth. It dissolves readily in water and also in boiling methyl alcohol, and separates from the latter, on long keeping, in almost colourless crusts. It is sparingly soluble in cold acetic acid, but dissolves readily on warming, and the concentrated solution gives, on the addition of sulphuric acid, at first a crimson coloration, but this soon changes to deep violet and, on adding a

little water, the colour becomes intense methylene-blue and then deep green.

*Methyl*iso*anhydrodihydrocryptopine*, $C_{22}H_{25}O_4N$,



This substance is obtained when either anhydrodihydrocryptopine *A* or *B* methosulphate is boiled with methyl-alcoholic potassium hydroxide, and the process seems to take place with the greater readiness when the methosulphate of *A* is employed. The methosulphate, *A* (5 grams), is finely powdered, moistened with methyl alcohol, mixed with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.), and heated on the steam-bath in an open flask for twenty to twenty-five minutes just to boiling. It is then vigorously boiled, so that the bulk of the methyl alcohol may escape and, during this operation, much of the methyl*iso*anhydrodihydrocryptopine separates as a pasty mass. The cold product is diluted with water, the solid collected, well washed, drained on porous porcelain, and dissolved in boiling methyl alcohol, from which the new substance separates in warty masses or bundles of needles. After two more crystallisations, and so soon as the pale yellow mother liquor has been entirely removed, the substance is obtained in colourless needles which exhibit a striking and beautiful lilac fluorescence. The decomposition of the methosulphate of anhydrodihydrocryptopine (*B*) was carried out under the same conditions, and the substance obtained had properties which were identical with those of the methyl*iso*anhydrodihydrocryptopine prepared from the methosulphate of *A* :

0·1131 gave 0·2982 CO_2 and 0·0693 H_2O. C = 71·8; H = 6·8.
0·3400 „ 11·4 c.c. N_2 at 13° and 747 mm. N = 3·9.
$C_{22}H_{25}O_4N$ requires C = 71·9; H = 6·8; N = 3·8 per cent.

*Methyl*iso*anhydrodihydrocryptopine* melts at 106° and is sparingly soluble in alcohol and still less so in methyl alcohol; it dissolves readily in benzene, ethyl acetate, acetone, or chloroform, but is sparingly soluble in light petroleum. The solution of a trace in a drop of acetic acid gives, on the addition of sulphuric acid, an intense crimson coloration.

The salts of this base are very readily soluble in water, and exhibit little facility for crystallising. The hydrochloride, sulphate, and nitrate have a tendency to separate from concentrated solu-

tions as gums and, even when potassium iodide is added to the solution of the hydrochloride, the milky liquid deposits a gum, but this dissolves in boiling water and, on cooling and rubbing, crystallisation gradually sets in. Mercuric chloride gives, with the hydrochloride, a caseous precipitate which melts to a gum under boiling water; auric chloride yields a drab-purple, amorphous precipitate. The *platinichloride* is obtained as an ochreous precipitate which rapidly becomes crystalline when platinic chloride is added to the hot solution of the hydrochloride. It darkens at 190° and decomposes at 195—200° with evolution of gas and formation of a brown froth:

0·2355 gave 0·0402 Pt. Pt = 17·1.

$(C_{22}H_{25}O_4N)_2H_2PtCl_6$ requires Pt = 17·0 per cent.

Methylisoanhydrodihydrocryptopine Methosulphate, $C_{22}H_{25}O_4N,Me_2SO_4$.—The base is readily soluble in benzene, and when mixed with an equal weight of methyl sulphate the solution clouds, crystallisation soon sets in, and the whole becomes a paste of crystals of the methosulphate. This was collected, washed thoroughly with benzene, dried on porous porcelain, and recrystallised from water, in which it is rather sparingly soluble and from which it separates in colourless, flat needles:

0·3109 gave 7·5 c.c. N_2 at 13° and 756 mm. N = 2·8.

0·2844 „ 0·1396 $BaSO_4$. S = 6·7.

$C_{22}H_{25}O_4N,Me_2SO_4$ requires N = 2·8; S = 6·5 per cent.

This methosulphate softens at 210° and melts at 215° to a transparent syrup. It dissolves freely in boiling methyl alcohol and separates, on slowly cooling, in colourless groups of needles which have a pale lilac fluorescence; it readily forms supersaturated solutions, both with water and methyl alcohol. A trace of the substance, moistened with acetic acid, gives with sulphuric acid a port-wine coloration.

The Methiodide, $C_{22}H_{25}O_4N,MeI$.—The hot solution of the methosulphate gives, on the addition of potassium iodide, a milky precipitate which soon crystallises in microscopic, feathery groups of needles. It dissolves readily in hot water and separates, on cooling, in small needles; it is also soluble in hot alcohol, from which it crystallises well in groups of slender, prismatic needles. When rapidly heated it melts with effervescence at 215—217° to an amber syrup:

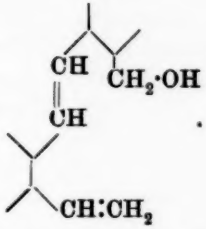
0·1102 gave 0·2188 CO_2 and 0·0564 H_2O. C = 54·1; H = 5·7.

$C_{23}H_{28}O_4NI$ requires C = 54·2; H = 5·5 per cent.

The *methochloride*, prepared by the action of silver chloride on

the hot solution of the iodide in the usual manner, is very readily soluble, and remains, on evaporating the solvent, as a shellac-like mass containing crystalline nodules.

*α- and β-*iso*Cryptopidol*, $C_{20}H_{20}O_5$,



These substances are obtained when methyl*iso*anhydrodihydrocryptopine methosulphate is treated with methyl-alcoholic potassium hydroxide, but the decomposition takes place with difficulty and, after several experiments, the following procedure was found to give the best results.

The finely powdered methosulphate (5 grams) was mixed in an open flask with methyl-alcoholic potassium hydroxide (50 c.c. of 25 per cent.) and heated in boiling water, when a clear solution was produced and trimethylamine was slowly disengaged. After five hours the flask was transferred to an oil-bath and heated at 130° for an hour and a half and, after cooling, water was added and the rather viscid, ochreous precipitate collected, washed with water, and dried on porous porcelain.

The powdered mass was then repeatedly extracted with boiling methyl alcohol (*A*) until the whole of the *α*-iso*cryptopidol*, which is present in by far the larger proportion, had been dissolved out, leaving the crude *β-iso*cryptopidol as a hard, ochreous mass. This was dried, dissolved in hot methyl ethyl ketone, filtered from inorganic impurity, and the filtrate mixed with much water and heated on the steam-bath until the methyl ethyl ketone had been removed. The pale brown resin, which on cooling became quite hard and similar to shellac in appearance, was ground, warmed with methyl alcohol to remove possible traces of the *α*-modification, and the ochreous precipitate collected, dried in the steam-oven, and analysed:

0·1066 gave 0·2768 CO_2 and 0·0595 H_2O. C = 70·8; H = 6·2.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

β-iso*Cryptopidol* softens somewhat at 230°, but is not melted at 260°; its solution in acetic acid gives with sulphuric acid an intense port-wine coloration. It is sparingly soluble in most organic solvents, but dissolves readily in hot acetic anhydride, apparently without the formation of an acetyl derivative, since, after boiling for ten minutes with a large excess of acetic anhydride, evaporating

away most of the reagent, cooling, and adding methyl alcohol, a chalky precipitate was obtained, which gave on analysis C=70·7; H=6·1, and possessed all the properties of the original substance.

α-iso*Cryptopidol*.—The methyl-alcoholic solution (*A*) from the purification of the β-isomeride, was concentrated and left in the ice-chest, when an indistinctly crystalline powder gradually separated in large quantity, which was collected, and more was obtained from the mother liquor by treatment with animal charcoal, concentrating, and adding a little water.

The whole was then twice recrystallised from methyl alcohol with the addition of a little glacial acetic acid to remove any trace of basic impurity. The granular, crystalline precipitate was then dried over phosphoric oxide in a desiccator:

0·1044 gave 0·2706 CO_2 and 0·0578 H_2O. C=70·7; H=6·1.

$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

α-iso*Cryptopidol* melts at 90—92°, and a trace, dissolved in a drop of acetic acid, gives, on the addition of sulphuric acid, an intense reddish-violet coloration.

I. *The Conversion of Anhydrodihydrocryptopine* (*B*) *into Hydroxytetrahydroanhydrocryptopine* (compare pp. 864, 865) *by the Action of Dilute Hydrochloric or Sulphuric Acids.*

The action of dilute hydrochloric acid on anhydrodihydrocryptopine (*B*, m. p. 127°) (p. 941) is very slow on account of the sparing solubility of the hydrochloride in dilute hydrochloric acid, and the best results were obtained under the following conditions: The base (5 grams) was ground to a paste with water (100 c.c.) and mixed with concentrated hydrochloric acid (9 c.c.), when the sparingly soluble hydrochloride immediately separated. After heating on the steam-bath for three days the product was left in the ice-chest for a week and the comparatively small quantity of the sparingly soluble hydrochloride collected. This was recrystallised from water and decomposed by ammonia, when it yielded a colourless base which, after recrystallisation from methyl alcohol, melted at 127—128° and consisted of anhydrodihydrocryptopine (*B*), as the mixed melting point and careful comparison showed. The filtrate from the sparingly soluble hydrochloride gave, with sodium hydroxide, a grey, amorphous precipitate in quantity, and this became chalky on keeping; it was collected, washed well, dissolved in a little dilute hydrochloric acid, and the solution left in the ice-chest for a week, when only a very small quantity of the hydrochloride of anhydrodihydrocryptopine (*B*) separated and was removed. After again precipitating with sodium hydroxide, the

base was extracted with ether, in which it is readily soluble to an almost colourless solution with a pale blue fluorescence, the ethereal solution was filtered from a black, flocculent substance, dried over potassium carbonate, and evaporated, when a pale yellow resin remained. This was dissolved in methyl alcohol, the solution precipitated by water, and the chalky base dried over phosphoric oxide:

0·1138 gave 0·2776 CO_2 and 0·0734 H_2O. C = 68·1; H = 6·7.

$C_{21}H_{25}O_5N$ requires C = 68·0; H = 6·7 per cent.

Hydroxytetrahydroanhydrocryptopine melts at about 75° and has, so far, not been obtained in the crystalline condition; it dissolves readily in acetic acid and gives, on the addition of sulphuric acid, a pale yellow solution which on dilution with a little water becomes green. The hydrochloride and most of the other salts are readily soluble, and the most characteristic salts are the sulphate and iodide, and these are described below. The *platinichloride* is obtained, on the addition of platinic chloride to the warm dilute solution of the hydrochloride, as a chalky, drab precipitate:

0·1032 gave 0·1665 CO_2 and 0·0433 H_2O. C = 44·0; H = 4·6.

0·2006 „ 0·0335 Pt. Pt = 16·7.

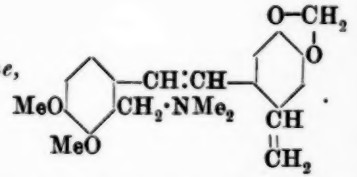
$(C_{21}H_{25}O_5N)_2,H_2PtCl_6$ requires C = 43·7; H = 4·5; Pt = 16·9 per cent.

II. *Action of Dilute Sulphuric Acid on Anhydrodihydrocryptopine (B).*

This process of hydration proceeds more smoothly than that just described, in which dilute hydrochloric acid was used, probably because the sulphate of anhydrodihydrocryptopine (*B*) is more readily soluble than the hydrochloride. The base (4 grams), made up to a paste with water (50 c.c.), was heated to boiling and mixed with a boiling solution of sulphuric acid (5 c.c.) in water (50 c.c.) when almost the whole dissolved immediately to a yellow solution. After boiling vigorously for half an hour in an open flask, in such a way that the solution was concentrated to 70 c.c., the deep yellow liquid was left in the ice-chest for several days and then decanted from the small sulphur-yellow groups of prisms which had separated and consisted of the sulphate of hydroxytetrahydroanhydrocryptopine mixed with a considerable proportion of the sulphate of anhydrodihydrocryptopine (*B*). The acid mother liquor was concentrated by distillation from the water-bath under 20 mm. pressure, and then allowed to remain exposed to the air for some weeks, when a mass of dark crystals gradually separated, which were collected and recrystallised several times from water. The pure *sulphate* of hydroxytetrahydroanhydrocryptopine thus ob-

tained is rather readily soluble in boiling water, but sparingly so in the cold, and separates as a mass of small, perfectly defined, four-sided prisms; it melts at about 150° to a yellow froth, and its solution in acetic acid gives with sulphuric acid a yellow colour which on dilution with a little water becomes green. The *iodide* is obtained by mixing boiling dilute solutions of the sulphate and potassium iodide, when a clear liquid results, from which the iodide separates as a granular precipitate consisting of irregular prisms; it melts at 155—158° with effervescence. Hydroxytetrahydroanhydrocryptopine was obtained from the sulphate, on the addition of ammonia, as a gelatinous precipitate which gradually hardened; it was dissolved in methyl alcohol and precipitated by water as a chalky mass. (Found, C = 67·7; H = 6·4, whereas $C_{21}H_{25}O_5N$ requires C = 68·0; H = 6·7 per cent.) Obviously this substance is the same as the base which had been obtained from the hydrochloride in experiment (I).

N-Dimethylisotetrahydroberberine,



This new base corresponds with the *N*-benzylmethyl*iso*tetrahydroberberine* described by McDavid, Perkin, and Robinson (formula VIII, T., 1912, **101**, 1221), and is prepared by the action of methyl-alcoholic potassium hydroxide on the methosulphate of *N*-methyl*iso*tetrahydroberberine (Base *B*).

The latter base was obtained by Pyman (T., 1913, **103**, 835) by the evaporation of the aqueous solution of tetrahydroberberine methohydroxide, but a more convenient method is to decompose tetrahydroberberine methosulphate with methyl-alcoholic potassium hydroxide. Twenty-five grams of tetrahydroberberine methosulphate (compare McDavid, Perkin, and Robinson, *loc. cit.*, p. 1222) are thoroughly mixed with methyl-alcoholic potassium hydroxide (150 c.c. of 25 per cent.) and heated in boiling water for twenty minutes when, on adding much water, a chalky precipitate separates which filters with difficulty, but readily so if the whole is allowed to remain for twenty-four hours. This is collected, washed well, dried on porous porcelain, and recrystallised from alcohol, from which it separates (16 grams) in glistening prisms which melt

* This substance is not named in that communication and it may be pointed out that the formula of its methiodide is incorrectly given on p. 1225 and should contain $-CH_2\cdot N(C_7H_7)Me_2I$ instead of $-CH_2\cdot N(C_7H_7)MeI$.

at 114—115° and consist of pure *N*-methyl*iso*tetrahydroberberine (Base *B*). The mother liquor was evaporated, and the brown syrup dissolved in dilute hydrochloric acid, when a small quantity (nearly 2 grams) of the sparingly soluble hydrochloride of Base *B* separated, so that the total yield was about 18·5 grams instead of the theoretically possible yield of 19·0 grams.

N-*Methyl*isotetrahydroberberine (B) *Methosulphate*, $C_{21}H_{23}O_4N,Me_2SO_4$.—In order to obtain this substance, Base *B* (5 grams), dissolved in warm benzene (20 c.c.) was mixed with methyl sulphate (5 c.c.) and the whole heated to boiling for a few seconds. Crystallisation commenced while still hot and, on stirring, the liquid became filled with balls of colourless needles, which were collected, washed thoroughly with benzene, dried on porous porcelain, and recrystallised from methyl alcohol:

0·2757 gave 0·1401 $BaSO_4$. S = 6·9.

$C_{23}H_{29}O_8NS$ requires S = 6·7 per cent.

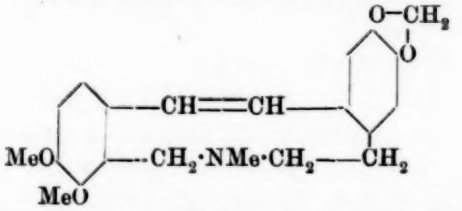
This methosulphate melts fairly sharply at 210—212°, and is readily soluble in hot methyl alcohol, from which it crystallises in well-defined prisms; it also dissolves readily in hot water, but much less so in the cold, and separates in thin laminæ. The addition of potassium iodide to the hot aqueous solution of the methosulphate produces a milky liquid, which soon crystallises and, after boiling for a few seconds, the *methiodide* was collected and dried in the steam-oven. It begins to discolour at 205° and melts at about 215—220° to a pale red syrup; it is very sparingly soluble in water, but readily so in boiling methyl alcohol, from which it separates as a crust of glistening prisms. The solution of a very small quantity in a few drops of acetic acid gives, on the addition of sulphuric acid, a yellow solution, which gradually becomes deep brownish-green and, on the addition of a little water, intense indigo-blue.

N-*Dimethyl*iso*tetrahydroberberine*.—This substance was prepared by digesting *N*-methyl*iso*tetrahydroberberine (*B*) methosulphate (14 grams), dissolved in the least quantity of boiling methyl alcohol, with methyl-alcoholic potassium hydroxide (70 c.c. of 25 per cent.) for ten minutes and, after boiling away most of the methyl alcohol, water was added, when a viscid precipitate separated which was extracted with ether. The ethereal solution, which exhibited a pale lilac fluorescence, was washed with water until quite free from methyl alcohol, dried over potassium carbonate, concentrated to a small bulk, and left in the ice-chest, when the new base separated in colourless needles:

0·1056 gave 0·2799 CO_2 and 0·0662 H_2O. C = 72·3; H = 7·0.
0·4652 „ 14·9 c.c. N_2 at 14° and 760 mm. N = 3·9.
$C_{22}H_{25}O_4N$ requires C = 71·9; H = 6·8; N = 3·8 per cent.

N-*Methyl*isotetrahydroberberine melts at 98—100° and closely resembles methyl*iso*anhydrodihydrocryptopine (m. p. 106°, p. 945) in appearance and properties. Like the latter, the colourless crystals exhibit a striking and beautiful lilac fluorescence and give, with acetic acid and sulphuric acid, an intense port-wine coloration which becomes more violet on the addition of a little water. It is readily soluble in the usual organic solvents, and forms salts with mineral acids which are also readily soluble in water.

N-*Methyl*isotetrahydroberberine (*A*),



and its Conversion into N-*Dimethyl*isotetrahydroberberine.

The base (*A*) (m. p. 133°) employed in these experiments was prepared by the dehydration of tetrahydroberberine methohydroxide by evaporation in a vacuum according to the directions given by Pyman (T., 1913, **103**, 828), and several times recrystallised from ethyl acetate until it was quite free from base *B*, which is produced at the same time.

The *methosulphate*, $C_{21}H_{23}O_4N,Me_2SO_4$, was obtained by adding methyl sulphate (4 c.c.) to the hot solution of the base (5 grams) in benzene (20 c.c.), when the liquid soon clouded and deposited a gum which, on stirring, crystallised. After collecting, washing with benzene, and drying on porous porcelain, the substance was recrystallised from hot water, in which it is readily soluble and from which it separates in characteristic, round, warty masses:

0·3034 gave 0·1539 $BaSO_4$. S = 7·0.
$C_{23}H_{29}O_8NS$ requires S = 6·7 per cent.

N-*Methyl*isotetrahydroberberine (*A*) *methosulphate* melts at about 233° to a pale yellow syrup, and its hot aqueous solution gives, on the addition of potassium iodide, a viscid precipitate which melts under boiling water, but solidifies on rubbing. This *methiodide* dissolves readily in boiling methyl alcohol, and crystallises in glistening crusts, or, if the solution is allowed to cool slowly, in large, magnificent, glistening prisms which, in the steam-oven,

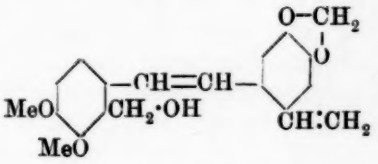
entirely lose their lustre and become chalky and brittle. It melts at 145—147° to a pale yellow syrup, which decomposes with effervescence about 200—205°:

0·1227 gave 0·2418 CO_2 and 0·0602 H_2O. C=53·7; H=5·5.

$C_{23}H_{28}O_4NI$ requires C=54·2; H=5·5 per cent.

N-*Dimethyl*iso*tetrahydroberberine* (m. p. 98—100°, compare p. 950).—This substance was readily obtained by boiling the *A*-methosulphate with methyl-alcoholic potassium hydroxide under the conditions described on p. 951, in the case of the *B*-isomeride. On dilution with water the product deposited a viscid mass, which crystallised from ether in colourless needles possessing a lilac fluorescence and melting at 98—100°, and the identity with the *N*-dimethyl*iso*tetrahydroberberine obtained from base *B* was proved by analysis. (Found, C=71·7; H=6·9; N=3·7. $C_{22}H_{25}O_4N$ requires C=71·9; H=6·8; N=3·8 per cent.) and by the fact that the mixture of the two specimens melted at 98—100°.

*α- and β-*iso*Berberidol*,



These isomeric substances are produced, together with trimethylamine, when *N*-dimethyl*iso*tetrahydroberberine methosulphate is decomposed by means of methyl-alcoholic potassium hydroxide, but the decomposition takes place with considerable difficulty. The methosulphate was obtained by dissolving *N*-dimethyl*iso*tetrahydroberberine (3 grams) in benzene (10 c.c.), adding methyl sulphate (3 c.c.), and allowing to remain, when combination took place with rise of temperature and apparently with more readiness than usual, and in a short time the whole set to a semi-solid, crystalline mass. After collecting, washing with benzene, and drying on porous porcelain, the substance was dissolved in a little hot water, from which it separated as a voluminous mass of microscopic needles possessing a slight lilac fluorescence:

0·3137 gave 0·1522 $BaSO_4$. S=6·6.

$C_{22}H_{25}O_4N,Me_2SO_4$ requires S=6·5 per cent.

N-*Dimethyl*iso*tetrahydroberberine methosulphate* shrinks at 175—180° and melts at about 210° to a pale yellow syrup, and the solution of a trace in acetic acid gives with sulphuric acid a port-wine coloration which, on the addition of a little water, becomes permanganate colour. The aqueous solution of the methosulphate gives, on the addition of potassium iodide, a milky liquid which

deposits a colourless syrup; this solidifies on stirring, and is very readily soluble in methyl alcohol, from which it crystallises with difficulty.

*α- and β-*iso*Berberidol.*—In preparing these isomerides the methosulphate just mentioned (4 grams), dissolved in hot methyl alcohol (10 c.c.), was mixed with methyl-alcoholic potassium hydroxide (25 c.c. of 35 per cent.) and heated in a flask connected with a beaker containing dilute hydrochloric acid for three hours in boiling water and then for two hours in an oil-bath at 135°, most of the methyl alcohol being allowed to distil over. The acid distillate in the beaker was evaporated nearly to dryness, mixed with platinic chloride, and left over sulphuric acid, when the characteristic crystals of trimethylamine platinichloride gradually separated. The cloudy residue on the flask yielded, on dilution with much water, a chalky precipitate which, after collecting and thoroughly washing with water, had the consistency of soft rubber. When this was digested with methyl alcohol most of the α-modification readily dissolved, and the relatively small residue became granular and consisted of the crude β-isomeride. This was powdered, again extracted with hot methyl alcohol, dissolved in a little boiling methyl ethyl ketone, filtered, and mixed with methyl alcohol when, on exposure to the air, crusts separated which were scarcely crystalline:

0·1238 gave 0·3201 CO_2 and 0·0679 H_2O. C = 70·5; H = 6·1.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

This specimen of *β-iso*berberidol began to soften at 245° and melted indefinitely at about 275°, whereas the substance obtained by McDavid, Perkin, and Robinson (T., 1912, **101**, 1226) by the action of alcoholic potassium hydroxide on *N*-benzylmethyl*iso*tetrahydroberberine methochloride, which is presumably the same substance, began to decompose at 250° and melted at about 275°. The methyl-alcoholic solution containing the α-modification was concentrated, mixed with dilute hydrochloric acid in order to remove possible basic impurity, the precipitate collected, washed, dried on porous porcelain, and crystallised from hot methyl alcohol, in which it is rather sparingly soluble, and from which it separates, especially on stirring, in nearly colourless, crystalline crusts or sometimes in the form of needles:

0·1047 gave 0·2725 CO_2 and 0·0598 H_2O. C = 71·0; H = 6·3.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 6·0 per cent.

α-iso*Berberidol* melts at 90°, and is readily soluble in benzene, chloroform, acetone, or acetic acid, but sparingly so in ether or light petroleum.

The solution in acetic acid gives, on the addition of sulphuric

acid, an intense claret coloration. In order to attempt the preparation of an acetyl derivative, *α-iso*berberidol was dissolved in warm acetic anhydride and the colourless solution gently boiled for five minutes by means of a sulphuric acid-bath; most of the excess of anhydride was then boiled away, and the cold residue mixed with an equal volume of methyl alcohol when, on cooling to −10° and stirring, the whole set to a mass of crystals, which melted at 88—90° and consisted of unchanged *α-iso*berberidol as the analysis showed (Found, C=70·0; H=6·1), and also the fact that a mixture with the original substance melted at the same temperature. A curious result was obtained when some *α-iso*berberidol, after treatment with acetic anhydride in the manner just described, was accidentally heated to a final temperature of 230° in the sulphuric acid-bath. The residue, dissolved in acetic anhydride and mixed with methyl alcohol, yielded a rather viscid precipitate which, when digested with methyl alcohol, became chalky, but did not dissolve. The precipitate, collected and washed thoroughly with hot methyl alcohol, sintered at about 200° and melted at about 215° to an amber resin, and this substance is also a polymeride of *α-iso*berberidol (Found, C=70·2; H=6·2), but is evidently distinct from *β-iso*berberidol, which, however, it closely resembles. In another experiment *α-iso*berberidol (1 gram) was heated in a sealed tube with acetyl chloride (5 c.c.) in boiling water for two hours and the brown solution evaporated, when a viscid residue remained, which gradually hardened and was almost insoluble in boiling methyl alcohol, under which it melted to a rubbery mass which again consisted of a polymeride. (Found, C=70·2; H=6·1.) It is obvious from these experiments that the tendency for *α-iso*berberidol to polymerise under the influence of acid reagents is very marked, whereas its method of preparation shows that alkalis bring about this change only in a comparatively slight degree.

Oxidation of α-iso*Berberidol.*

In this oxidation, *α-iso*berberidol (5 grams) was dissolved in acetone (200 c.c.) and, after cooling to −10°, very finely powdered permanganate was added in small quantities at a time, the whole process taking about two hours. The product was filtered, the manganese precipitate thoroughly washed with acetone, and the nearly colourless acetone filtrate evaporated, when a pale yellow syrup remained, which soon began to deposit crystals and in a few days become semi-solid. After remaining in contact with porous porcelain, the viscid mass was washed with ether, the residue dissolved in much ether, filtered, and the solution concentrated considerably, when lemon-yellow crusts of needles gradually separated

which melted at 88—90° and consisted of unchanged *α-iso*berberidol. The porous plate employed in the purification of the crude product was extracted with ether in a Soxhlet apparatus and the extract combined with the ethereal mother liquor, from which the *α-iso*berberidol had crystallised, the ether being then distilled off. When the residue, dissolved in a little methyl alcohol, was mixed with a concentrated aqueous solution of semicarbazide hydrochloride (3 grams) and sodium acetate (2·5 grams), a sparingly soluble semicarbazone commenced to separate at once. After twenty-four hours in the ice-chest this was collected (*A*) and washed with methyl alcohol, when it melted sharply at 203° without decomposition, and the mother liquor deposited on keeping a further small crop of the same semicarbazone. This substance is the *semicarbazone* of *ω-hydroxy*-3:4-*dimethoxy*-o-*tolylacetaldehyde*,

$$(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2:$$

0·1022 gave 0·2045 CO_2 and 0·0577 H_2O. C = 54·4; H = 6·3.

0·1245 „ 17·1 c.c. N_2 at 18° and 740 mm. N = 15·4.

$C_{12}H_{17}O_4N_3$ requires C = 53·9; H = 6·4; N = 15·7 per cent.

In attempting to hydrolyse this semicarbazone, the same difficulties were encountered as had been met with in the case of the semicarbazone of 4:5-dimethoxy-2-vinylbenzaldehyde (p. 904), and these were overcome by recourse to the same expedient. The semicarbazone (4 grams) was dissolved in pyruvic acid (10 c.c.) and heated on the steam-bath for two minutes when, on keeping, the brown liquid deposited crystals of the semicarbazone of pyruvic acid. Water was added, the cloudy liquid extracted with much ether, the pale yellow ethereal solution washed thoroughly with water and sodium carbonate, dried over potassium carbonate, and evaporated. The residual yellow syrup (3 grams) gradually solidified to a silky mass of needles and, after leaving in contact with porous porcelain, the mass was dissolved in pure dry ether, in which it is moderately readily soluble; the solution was then concentrated and cooled in a freezing mixture, when groups of needles separated. After rapidly collecting on a cooled funnel by the aid of the pump and washing with a little very cold ether, the colourless substance was dried over phosphoric oxide:

0·1019 gave 0·2344 CO_2 and 0·0602 H_2O. C = 62·7; H = 6·7.

0·1079 „ 0·2498 CO_2 „ 0·0646 H_2O. C = 63·1; H = 6·6.

$C_{11}H_{14}O_4$ requires C = 62·8; H = 6·6 per cent.

ω-Hydroxy-3:4-*dimethoxy*-o-*tolylacetaldehyde*,

$$(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CHO,$$

melts at 56—58°, is readily soluble in most organic solvents, and shows properties characteristic of a substituted phenylacetaldehyde.

The *oxime*, $(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CH{:}N\cdot OH$, was prepared

by adding a concentrated aqueous solution of hydroxylamine hydrochloride (0·6 gram) and sodium acetate (0·5 gram) to the hot solution of the substance (0·5 gram) in methyl alcohol (10 c.c.), and after gently boiling for five minutes the whole was allowed to remain for two days. The addition of water produced a milky liquid, which soon deposited the oxime as a voluminous mass of needles and, after extracting with ether, the ethereal solution was thoroughly washed with water, dried, and concentrated to a small bulk, when a small, crystalline crust separated. The ethereal mother liquor was decanted, evaporated, and the rather viscid residue crystallised from benzene containing a little light petroleum, from which the same substance separated in stars composed of thin laminæ:

0·1067 gave 0·2305 CO_2 and 0·0648 H_2O. C = 58·9; H = 6·7.
0·2164 „ 12·3 c.c. N_2 at 12° and 747 mm. N = 6·6.
$C_{11}H_{15}O_4N$ requires C = 58·7; H = 6·7; N = 6·2 per cent.

ω-Hydroxy-3:4-dimethoxy-o-tolylacetoxime melts at 105—106° and is readily soluble in alcohol, rather sparingly so in cold benzene, and almost insoluble in light petroleum. It is shown on p. 959 that the aldehyde is readily oxidised by permanganate with the formation of *ω-hydroxy-3:4-dimethoxy-o-tolylacetic acid*,

$$(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CO_2H.$$

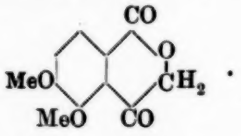
The manganese precipitate from the oxidation of α-berberidol (p. 955), containing the potassium salts, was repeatedly extracted with hot water, the extract evaporated until quite free from acetone, and filtered from a small amount of tar. On acidifying with hydrochloric acid until distinctly acid to Congo paper, a tarry substance separated, but, on boiling with much water, all dissolved with the exception of a small quantity of black resin, which was removed by filtration.

After the filtrate had been decolorised with animal charcoal it was evaporated somewhat under diminished pressure and extracted with much ether on the machine. When the carefully dried ethereal solution was concentrated and left in the ice-chest a small, colourless, crystalline crust separated, which crystallised from water, in which it is sparingly soluble, as a woolly mass of slender needles:

0·1072 gave 0·2345 CO_2 and 0·0429 H_2O. C = 59·7; H = 4·4.
$C_{11}H_{10}O_5$ requires C = 59·5; H = 4·5 per cent.

This substance melts at 188—190°, and is insoluble in dilute sodium carbonate or dilute sodium hydroxide in the cold, but it dissolves readily in the latter, on warming, to a yellow solution and exhibits all the properties of a lactone. The careful considera-

tion of its properties leaves no doubt that it is 4-*keto*-5:6-*dimethoxydihydro*isocoumarin, and is represented by the formula:



Titration: 0·0912 of the substance was mixed with 7 c.c. of *N*/10-NaOH, heated to boiling for a couple of minutes, and the excess of alkali determined by *N*/10-H_2SO_4, when it was found that 4·3 c.c. had been neutralised by the lactone, whereas the above amount of a substance, $C_{11}H_{10}O_5$, becoming monobasic, should neutralise 4·1 c.c. *N*/10-NaOH. When the neutral solution was acidified, a gelatinous precipitate separated, which was immediately soluble in cold dilute sodium carbonate, and evidently consisted of 3:4-dimethoxy-2-glycollylbenzoic acid,

$$(MeO)_2C_6H_2(CO_2H)\cdot CO\cdot CH_2\cdot OH,$$

but, on keeping for twenty-four hours, this had become converted into a mass of needles which were now insoluble in sodium carbonate, melted at 188—189°, and consisted of the keto*iso*coumarin. That this substance is a ketone was confirmed by the fact that its warm aqueous solution gives an immediate milkiness with *p*-bromophenylhydrazine acetate, and a viscid precipitate separates which, on rubbing, becomes crystalline. In order to obtain further evidence of the presence of the keto-group, the very small available quantity of substance was boiled with an excess of a solution of semicarbazide hydrochloride and sodium acetate, when the needles rapidly changed in appearance and a chalky precipitate of the *semicarbazone* separated. After collecting and washing, this derivative melted at 235—237° with evolution of gas to a red syrup and the analysis gave the following results:

0·0646 gave 8·2 c.c. N_2 at 10° and 742 mm. N = 14·9.

$C_{12}H_{13}O_5N_3$ requires N = 15·1 per cent.

The ethereal mother liquor from which the keto*iso*coumarin had separated was concentrated and left in the ice-chest for a week, but it did not deposit any further quantity of this substance; it was therefore evaporated, when a large amount of a pale yellow syrup resulted which was completely soluble in hot water, yielding a solution which clouded on cooling. The whole was dissolved in water, rendered strongly alkaline with ammonia, and boiled with barium chloride, when a small quantity of a heavy, sparingly soluble precipitate separated, which was collected and dissolved in boiling very dilute hydrochloric acid. The solution was then decolorised by animal charcoal and placed over sulphuric acid,

when a crystalline acid gradually separated which melted at about 178—183° with effervescence, and evidently consisted of hydrastic acid. (Found, C=50·9; H=3·1. $C_9H_6O_6$ requires C=51·4; H=2·9 per cent.)

The identity was confirmed by heating the acid at 180—190° until decomposition was complete and crystallising the anhydride from alcohol, when it melted at 175°, which is the melting point of the anhydride of hydrastic acid. The mother liquor from the sparingly soluble barium salt gave, with hydrochloric acid, a cloudy solution, from which an oil separated and, when the decanted solution was left in the ice-chest and frequently stirred, it became filled with glistening laminæ, and a further quantity of the same substance was obtained by boiling the oil with water and animal charcoal, concentrating, and keeping in the ice-chest. After recrystallisation from water, the following analytical results were obtained:

0·1060 gave 0·2271 CO_2 and 0·0596 H_2O. C=58·4; H=6·2.
0·0928 „ 0·2001 CO_2 „ 0·0517 H_2O. C=58·8; H=6·2.
$C_{11}H_{14}O_5$ requires C=58·4; H=6·2 per cent.

Titration: 0·2367 neutralised 10·1 c.c. *N*/10-NaOH, whereas this amount of a monobasic acid, $C_{11}H_{14}O_5$, should neutralise 10·4 c.c. *N*/10-NaOH. When the neutral solution was acidified, the acid gradually separated in long needles. This acid, which is evidently *ω-hydroxy*-3:4-*dimethoxy*-o-*tolylacetic acid*,

$$(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CO_2H,$$

melts at 125°, is sparingly soluble in cold water, and not very readily so even on boiling, and it usually separates as an oil which, however, rapidly crystallises on stirring and immediately on the introduction of a crystal. It is very soluble in methyl alcohol, chloroform, benzene, or formic acid, but almost insoluble in light petroleum, and crystallises well from benzene containing some light petroleum in groups of colourless needles.

When it is digested with acetic anhydride and the solution concentrated, cooled, and mixed with a little methyl alcohol, a crystalline crust separates which melts at 125° and evidently consists of the unchanged acid. In spite of the presence of the $-CH_2\cdot OH$ group, it appears, therefore, that this acid does not readily yield an acetyl derivative. In order to demonstrate that this acid corresponded with ω-hydroxy-3:4-dimethoxy-*o*-tolylacetaldehyde,

$$(MeO)_2C_6H_2(CH_2\cdot OH)\cdot CH_2\cdot CHO$$

(p. 956), the oxidation of the latter substance was undertaken. The aldehyde (0·5 gram), dissolved in acetone (30 c.c.), was gradually treated at the ordinary temperature with finely powdered permanganate (0·4 gram), but oxidation did not take place readily.

After remaining overnight, the product was mixed with water, the acetone evaporated, the filtrate and washings of the manganese precipitate concentrated and acidified, when the milky liquid, in contact with a crystal of ω-hydroxy-2:3-dimethoxy-*o*-tolylacetic acid, deposited a mass of needles. These were collected and recrystallised twice from water, when the substance melted at 125° and proved to be identical with the acid just mentioned, since a mixture of the two specimens melted at 125°.

Section VII.

The Methylcryptopines.

It is pointed out in the Introduction (p. 845) that cryptopine yields three methylcryptopines, $C_{22}H_{25}O_5N$, called α-, β-, and γ-, of widely different melting points: α- melts at 153°, β- at 128°, and γ- at 110°.

The first of these to be prepared was the modification γ, and this was obtained from cryptopine methochloride (p. 881) by the action of dilute sodium hydroxide. The methochloride (5 grams), dissolved in a little hot water, was mixed with *N*-sodium hydroxide (25 c.c.) and heated on the steam-bath, when the liquid soon clouded and deposited a yellow syrup which, on keeping in the ice-chest, gradually became semi-solid. After decanting the aqueous layer, the product was dissolved in ether, the ethereal solution washed, dried over potassium carbonate, and concentrated to low bulk when, on remaining in the ice-chest, brilliant crystals (2·2 grams) of methylcryptopine, γ, separated and, after rapidly washing with ether, melted at 110°. The mother liquor, left exposed to the air in a partly covered beaker, deposited 0·12 gram of the same substance and, on complete evaporation, a viscid syrup from which nothing crystalline could be isolated. Subsequently, a considerable amount of methylcryptopine, γ, was prepared from cryptopine methosulphate (p. 880) by boiling with aqueous potassium hydroxide. The methosulphate (5 grams), dissolved in water (50 c.c.), was mixed with 30 per cent. potassium hydroxide (5 c.c.), when the clear solution soon became milky and, on heating on the steam-bath, the milkiness greatly increased and a heavy, yellow syrup separated, which again only partly crystallised. After decanting the aqueous layer, the semi-solid mass was treated with ether in the manner just described, and yielded 2 grams of pure methylcryptopine, γ. A process which gives much better results and yields all the modifications of methylcryptopine has recently been worked out, and is as follows: Finely powdered cryptopine methosulphate (10 grams) is mixed with methyl alcohol (10 c.c.) and a

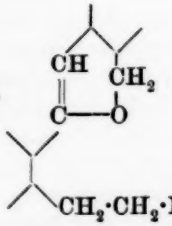
filtered solution of potassium hydroxide (6 grams) in methyl alcohol (20 c.c.) and heated on the steam-bath in an open flask for thirty minutes in such a way that much of the methyl alcohol boils away; the pale brown solution is then diluted with water (200 c.c.) and immediately extracted once with much ether.

The ethereal solution is washed until free from methyl alcohol, dried over potassium carbonate, and filtered, and it is essential that the whole operation shall be carried out as rapidly as possible, otherwise a good deal of methylcryptopine, α, will crystallise on the potassium carbonate and sides of the separating funnel. The filtered ethereal solution soon begins to deposit a crystalline precipitate of the nearly pure α-modification (m. p. usually about 146—148°), and more is obtained, sometimes along with a small quantity of the β-modification (m. p. 126—128°), on concentrating the mother liquor and allowing it to remain in the ice-chest. After filtering, the mother liquor is further concentrated, and then gradually deposits a soft, chalky crust mixed with large, pale yellow prisms, and these can be mechanically separated by means of a sieve.

The crust melts at 124—126°, and consists of the nearly pure β-modification, and the prisms melt at about 105° and are methylcryptopine (γ).

The final mother liquor deposits, on evaporation, a small amount of a yellow, uncrystallisable syrup, and the yields of the crystalline methylcryptopines vary considerably, but should be about 5 grams of α, 0·5 gram of β, and 1 gram of γ. This process proceeds, therefore, much more smoothly than the two first described, but, on the other hand, it gives a much smaller yield of the γ-modification.

The Methylcryptopines (α) *and* (β),



It has been shown in the Introduction (p. 845) that the methylcryptopines (α) and (β) are polymorphic modifications of the same substance (compare Sidgwick, T., 1915, **107**, 678), and the modification which is obtained in by far the larger proportion when cryptopine methosulphate is digested with methyl-alcoholic potassium hydroxide under the conditions just described is methylcryptopine (α):

0·1140 gave 0·2880 CO_2 and 0·0683 H_2O. C = 68·9; H = 6·6.
0·4704 „ 14·4 c.c. N_2 at 15° and 768 mm. N = 3·6.

$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

Methylcryptopine (α) melts at 151—153°, and is very sparingly soluble in ether, alcohol, ethyl acetate, or acetone in the cold, but dissolves comparatively readily in benzene. It may be dissolved in much boiling ethyl acetate or acetone, and the solutions may be concentrated very considerably without separation, but, on keeping or vigorous stirring, both solutions deposit crusts which melt at 151—153°. The solution in dilute sulphuric acid is colourless, but when heated in boiling water it soon becomes pink and, after remaining overnight, the intensely pink solution gives with ammonia an ochreous precipitate. Methylcryptopine (α) dissolves readily in dilute hydrochloric acid, and the addition of ammonia causes the separation of a gelatinous precipitate, which softens on warming to a mass like putty. When cooled in ice, this rapidly hardens, and may be ground up and washed and, after contact with porous porcelain, this curious substance melts in the steam-oven and solidifies on cooling to a resin which melts at about 75°. When, however, the gelatinous precipitate is extracted with much ether and the ethereal solution dried over potassium carbonate and concentrated, a granular precipitate separates, which melts at 150—152° and consists of methylcryptopine (α).

Conversion of Methylcryptopine (α) *into Methylcryptopine* (β).

This change was first brought about by heating the modification (α) (1 gram) with methyl alcohol (15 c.c.) in a sealed tube in the water-bath with frequent shaking, when the crystals gradually dissolved and, after half an hour, the tube was allowed to cool slowly in the water, during which magnificent, glistening prisms separated which became chalky in the steam-oven, melted at 127—128°, and consisted of methylcryptopine (β). The same change may be brought about by boiling a small quantity of (α) with much methyl alcohol, in which it, and also (β), is very sparingly soluble, and as soon as solution is complete, concentrating to low bulk and allowing to remain. Even when methylcryptopine (α) is boiled with much less than sufficient methyl alcohol to dissolve it completely, the conversion into (β) soon seems to be complete, for not only does the substance which crystallises from the filtered liquid melt at 126°, but the residue also exhibits the same melting point. Both sets of crystals, if exposed to the air for an hour or two, melt at 126° with effervescence, whereas, after drying in the steam-oven until constant, they melt at the same temperature without effervescence. As this behaviour, and the fact that the

crystals became chalky in the steam-oven, pointed to their containing solvent of crystallisation, a specimen which had been exposed to air for two hours was heated in the steam-oven until constant, when it lost 6·9 per cent., whereas $C_{22}H_{25}O_5N$,MeOH contains MeOH = 7·7 per cent.

After some of the same specimen had remained for three days exposed to air, the loss at 100° was only 2·8 per cent., so that the solvent of crystallisation evidently gradually escapes on exposure. The analysis of the substance, dried at 100° until constant, gave the following results:

0·1110 gave 0·2799 CO_2 and 0·0652 H_2O. C = 68·8; H = 6·5.
0·1122 „ 3·6 c.c. N_2 at 15° and 760 mm. N = 3·7.
$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

Methylcryptopine (β) melts at 127—128°, and is very sparingly soluble even in much boiling methyl alcohol, but dissolves more readily in boiling ethyl alcohol, and separates on cooling as a hard, granular precipitate; it is also sparingly soluble in ether or benzene, but dissolves more readily in acetone or ethyl acetate. The solution of a crystal in a drop of glacial acetic acid gives, on the addition of sulphuric acid, an orange-red coloration which becomes deep brown on keeping and intense brownish-violet on the addition of a few drops of water. When, however, a few drops of sulphuric acid are added to the solution in much acetic acid, no coloration is produced until the test-tube is placed in boiling water, when the solution becomes first yellow and then pale pink.

The solution in cold acetic anhydride gives a yellow coloration with sulphuric acid, which gradually becomes deep reddish-brown and, on placing in boiling water, a green colour develops. The chloroform solution of the substance decolorises bromine, but gives no green coloration, and in this and the other reactions just described, methylcryptopine (β) differs very markedly from methylcryptopine (γ) (compare p. 966).

Methylcryptopine (β) dissolves in dilute sulphuric acid to a colourless solution and, if the test-tube is placed in boiling water, a pink colour gradually develops, which rapidly increases in intensity and, after remaining for an hour, the deep permanganate solution gives with ammonia a chalky, ochreous precipitate (compare p. 872). The base also dissolves in concentrated nitric acid in the cold to a reddish-brown solution and, on diluting and warming, an ochreous precipitate separates which is very sparingly soluble in water, but readily so in dilute ammonia.

The conversion of methylcryptopine (β) into the modification (α) is readily accomplished by dissolving (β) in dilute hydrochloric acid, adding ammonia, and extracting with ether, when the ethereal

solution, after drying over potassium carbonate and concentrating, deposits a crust melting at 150—152°, and this consists of pure methylcryptopine (α).

Salts of Methylcryptopine (β).—The addition of dilute hydrochloric acid to the powdered base causes the formation of a rather sparingly soluble *hydrochloride*, and this dissolves in hot water and separates as a colourless, almost gelatinous precipitate, which dries to a horny mass on porous porcelain and melts, with effervescence, at about 180—182°.

The *sulphate* is also sparingly soluble, and separates from hot water as a gelatinous mass; the *nitrate* is obtained as a viscid mass, when dilute nitric acid is added to the base, which dissolves in hot water and separates, on cooling, as a flocculent precipitate. The *hydriodide* is precipitated, on the addition of potassium iodide to the warm solution of the hydrochloride, as a gum which, on heating, becomes a chalky, crystalline precipitate very sparingly soluble even in boiling water. It was collected, washed with methyl alcohol, and dried in the water-oven, when it melted at about 230—235°:

0·1112 gave 0·2095 CO_2 and 0·0536 H_2O. C = 51·3; H = 5·3.
$C_{22}H_{25}O_5N$,HI requires C = 51·6; H = 5·1 per cent.

The *platinichloride* is obtained, on the addition of platinic chloride to the dilute solution of the hydrochloride, as a pale salmon, amorphous precipitate which, on warming, becomes crystalline and deeper in colour; it is soluble in much water, and crystallises on cooling. After drying in the steam-oven, the salt became grey at 190°, very dark at 200°, and decomposed at about 210—215°, with effervescence, to a black mass:

0·2192 gave 0·0357 Pt. Pt = 16·2.
$(C_{22}H_{25}O_5N)_2H_2PtCl_6$ requires Pt = 16·6 per cent.

Methylcryptopine (β) *Methosulphate.*—The solution of methylcryptopine (β) (1 gram) in warm benzene (10 c.c.) gives, on the addition of *neutral* methyl sulphate (1 c.c.), a clear liquid which soon clouds, becomes warmer, and deposits a viscid syrup. After decanting the benzene, washing the syrup with this solvent, and removing the remainder of the latter by blowing in air, the viscid mass * was rubbed with much water when the methosulphate rapidly separated, in an almost pure condition, as a sparingly

* Unless methyl sulphate which has been left in contact with anhydrous potassium carbonate for several days is employed in this preparation, the viscid methosulphate soon becomes violet and in a day or two is converted into a deep violet varnish and the same applies in still greater degree to the case of the methosulphate of methylcryptopine (γ) (p. 967).

soluble, crystalline powder. This was collected, washed with water, dried on porous porcelain, and recrystallised from methyl alcohol:

0·4445 gave 0·2118 $BaSO_4$. S = 6·5.

$C_{22}H_{25}O_5N,Me_2SO_4$ requires S = 6·2 per cent.

Methylcryptopine (*β*) *methosulphate* scarcely discolours at 250°, becomes brown at 265°, and melts at about 275° with evolution of gas to a brown froth. It is very sparingly soluble in cold water, but dissolves on boiling, and separates as a very finely divided, chalky precipitate.

It dissolves, although not very readily, in hot methyl alcohol and crystallises, on cooling, as a voluminous mass of microscopic needles.

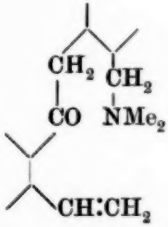
The hot aqueous solution gives, on the addition of potassium iodide, a milky liquid and, on boiling, the iodide separates as a voluminous, chalky precipitate. A trace of the methosulphate, dissolved in acetic acid, gives, on the addition of sulphuric acid, a deep yellow coloration which does not appear to change on keeping. The behaviour of this methosulphate towards methyl-alcoholic potassium hydroxide is described on p. 973.

Attempt to Prepare an Oxime or Semicarbazone of Methylcryptopine (*β*).

It is explained in the Introduction (p. 848) that it was important to determine whether methylcryptopine (*β*) contained a carbonyl group, and several experiments were therefore made with this object in view, of which the following only need be mentioned. When the solution in a slight excess of dilute acetic acid is heated on the steam-bath with excess of semicarbazide hydrochloride and sodium acetate and, after remaining overnight, the product is rendered alkaline with ammonia and extracted with much ether, the ethereal solution, after drying and concentrating, deposits almost the whole of the substance in the form of methylcryptopine (*α*) melting at 148—150°, but the last ethereal mother liquors always yield a very small quantity of a crystalline substance, which is almost insoluble in boiling methyl alcohol and melts at 197—200° with evolution of gas. This substance contains 7·0 per cent. of nitrogen, and is therefore not the semicarbazone, $C_{23}H_{28}O_5N_4$, which requires N = 12·7 per cent., but the quantity obtained was too small to allow of its nature being investigated. A mixture of equal weights of methylcryptopine (*β*), semicarbazide hydrochloride, and crystallised sodium acetate dissolves in hot water, and the solution, after heating at 50° for two hours and leaving for two days, yields, on the addition of ammonia and extraction with ether, almost the whole of the substance in the form of methylcryptopine (*α*), but a

very small quantity of the substance melting at 197—200° is also produced. In an attempt to prepare the oxime, equal weights of methylcryptopine (β), hydroxylamine hydrochloride, and crystallised sodium acetate were dissolved in hot water and, after leaving for three days, ammonia was added and the whole extracted with ether, the ethereal solution dried over potassium carbonate and concentrated, but it is curious that in this case nothing separated on keeping. When the ether was evaporated a gummy residue was left which contained N = 4·5, whereas the oxime, $C_{22}H_{26}O_5N_2$, requires N = 7·0 per cent. On rubbing with dry ether, a chalky powder was deposited which melted at 146—149° and consisted of methylcryptopine (α), the mother liquor yielded a further quantity of this mixed with some methylcryptopine (β), and ultimately almost the whole was recovered in this way. It would therefore seem that methylcryptopine (β) is not capable of yielding either an oxime or a semicarbazone.

Methylcryptopine (γ),



The preparation of this substance from cryptopine methochloride and methosulphate by the action of aqueous sodium hydroxide or methyl alcoholic potassium hydroxide is described on pp. 960, 961, and, for analysis, the substance was recrystallised from ether:

0·1026 gave 0·2591 CO_2 and 0·0602 H_2O. C = 68·8; H = 6·5.

0·1147 „ 3·7 c.c. N_2 at 17° and 753 mm. N = 3·5.

$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

Methylcryptopine (γ) melts at 110°, is sparingly soluble in methyl alcohol in the cold, but readily so on boiling, and separates as a colourless, crystalline powder consisting of well-developed prisms.

It is rather sparingly soluble in ether, and crystallises from this solvent in hard crusts of brilliant prisms; it also crystallises well from acetone, in which it is readily soluble. When a weak solution of bromine in chloroform is added to the solution of the substance in the same solvent a deep green colour develops which, on warming, becomes more intense and, on the further addition of bromine, changes to brown.

The solution in much acetic acid gives, on the addition of a few drops of sulphuric acid, a yellow colour which soon becomes

brownish-yellow and, on placing the test-tube in boiling water, an intense blackish-green is produced which gradually changes to violet-black. If to a trace of the substance, dissolved in cold acetic anhydride, a drop of sulphuric acid is added, an intense permanganate colour is first produced which, on warming, becomes deep sage-green. The solution of the substance in cold dilute sulphuric acid (1 in 10) is colourless, but, on heating on the steam-bath, it becomes pink and then deep permanganate colour, and the solution gives with ammonia an ochreous precipitate; a similar change takes place when the substance is boiled with hydrochloric acid (compare p. 869).

Salts of Methylcryptopine (γ).—The salts of this base differ from those of methylcryptopine (β) in that they are more readily soluble in water. When the base is rubbed with cold dilute sulphuric acid it dissolves readily, and the solution may remain clear for hours; if, however, the containing vessel is vigorously scratched or a crystal is introduced, the *sulphate* rapidly separates in groups of microscopic needles. It is readily soluble in water, but much less so in dilute sulphuric acid. The *hydrochloride* is also readily soluble and yields, on the addition of potassium iodide, a milky liquid which soon deposits a pale yellow syrup. This dissolves in boiling water and, on rubbing, the hydriodide separates in groups of flat needles:

0·1222 gave 0·2316 CO_2 and 0·0589 H_2O. C = 51·6; H = 5·3.
$C_{22}H_{25}O_5N,HI$ requires C = 51·6; H = 5·1 per cent.

This *hydriodide* melts at about 188° and dissolves, although with difficulty, in boiling alcohol, from which it separates as a glistening crust of well-defined, four-sided prisms. The *platinichloride*, prepared by the addition of platinic chloride to the warm solution of the hydrochloride, is a pale yellow, apparently crystalline precipitate, which becomes viscid on boiling with water and is soluble in hot alcohol:

0·1847 gave 0·3064 CO_2 and 0·0770 H_2O. C = 45·2; H = 4·6.
0·6415 „ 0·1068 Pt. Pt = 16·6.
$(C_{22}H_{25}O_5N)_2,H_2PtCl_6$ requires C = 44·9; H = 4·5; Pt = 16·6 per cent.

The Methosulphate.—Methylcryptopine (γ) (2·5 grams) dissolves readily in hot benzene (6 c.c.) and when mixed with neutral methyl sulphate (2 grams) considerable rise of temperature takes place, the solution suddenly clouds, and separates into two layers. The lower layer becomes a horny mass, but may be obtained crystalline by rubbing with a little methyl alcohol:

0·4445 gave 0·2118 $BaSO_4$. S = 6·5.
$C_{22}H_{25}O_5N,Me_2SO_4$ requires S = 6·2 per cent.

This salt is very unstable, and rapidly becomes purple on exposure to air; it is readily soluble in water or methyl alcohol.

The conversion of methylcryptopine (γ) into the *epi*methylcryptopines, by the action of boiling concentrated hydrochloric acid, is described on pp. 869 and 1019.

An attempt was made to reduce methylcryptopine (γ) by dissolving the substance (2 grams) in dilute sulphuric acid (100 c.c. of 20 per cent.) and adding a large excess of sodium amalgam (100 grams of 5 per cent.) in a basin which was finally heated on the water-bath. The solution was decanted from the mercury, cooled well, and mixed with excess of potassium hydroxide, when a semi-solid mass separated, which was extracted with ether. After drying over potassium carbonate, the ethereal extract was evaporated to a small bulk and left in the ice-chest, when glistening prisms separated (1·3 grams), which melted at 108—110° and consisted of unchanged methylcryptopine (γ).

Methylcryptopine (γ) *Oxime.*—This derivative was obtained by dissolving equal quantities of the base, hydroxylamine hydrochloride, and crystallised sodium acetate in boiling water and, after heating at 50° for two hours and leaving overnight, the clear solution was rendered strongly alkaline with ammonia, when a caseous precipitate separated which was extracted with ether. The ethereal solution was dried over potassium carbonate and evaporated, when a nearly colourless gum resulted which, after remaining over sulphuric acid in a vacuum desiccator for some days, yielded the following analytical results:

0·1211 gave 0·2966 CO_2 and 0·0719 H_2O. C = 66·7; H = 6·6.
0·1112 „ 6·9 c.c. N_2 at 14° and 760 mm. N = 6·6.
$C_{22}H_{26}O_5N_2$ requires C = 66·3; H = 6·5; N = 7·0 per cent.

There can thus be little doubt that this substance is the oxime of methylcryptopine (γ), although it was probably not quite pure, and very possibly contained as impurity some of the unchanged base.

Methylcryptopine (γ) *Semicarbazone.*—Methylcryptopine (γ) (2 grams) dissolves readily when it is added to a hot solution of semicarbazide hydrochloride (2 grams) and crystallised sodium acetate (2·5 grams), and if the liquid is heated at 50—60° for two hours and then left for several days, a crystalline crust separates in small quantity. This was collected, washed with water, and dried in the steam-oven, when it yielded, on analysis, numbers which indicate that it is the acetate of the hydrochloride of methylcryptopine (γ) semicarbazone:

0·1095 gave 0·2260 CO_2 and 0·0615 H_2O. C = 56·3; H = 6·2.
0·1121 „ 10·2 c.c. N_2 at 14° and 758 mm. N = 10·6.
0·2277 „ 0·0620 AgCl. Cl = 6·7.
$C_{23}H_{28}O_5N_4,C_2H_4O_2,HCl$ requires C = 55·9; H = 6·2; N = 10·4; Cl = 6·6 per cent.

This salt softens at 220° and melts at about 228—230° with decomposition to a dark brown resin; it is soluble in hot water and separates again with difficulty. The addition of potassium carbonate to the hot aqueous solution causes the semicarbazone to separate as a viscid precipitate, which was dissolved in much ether and, after drying over potassium carbonate, the concentrated ethereal solution was left in the ice-chest for some days, when a crystalline crust separated:

0·0627 gave 0·1456 CO_2 and 0·0369 H_2O. C = 63·3; H = 6·5.
0·1119 „ 11·6 c.c. N_2 at 13° and 751 mm. N = 12·0.
$C_{23}H_{28}O_5N_4$ requires C = 62·7; H = 6·4; N = 12·7 per cent.

Methylcryptopine (γ) *semicarbazone* melts at 185° without decomposition and is rather sparingly soluble in the usual organic solvents.

When the filtrate from the acetate of the hydrochloride was diluted with water and made alkaline with ammonia, a gelatinous precipitate separated which was extracted with much ether. The ethereal solution was dried over potassium carbonate, concentrated, and left in the ice-chest, when it deposited a considerable crust which melted at 183—185° and consisted of the semicarbazone. The ethereal mother liquor from this substance yielded, on evaporation, a syrup and, on rubbing this with methyl alcohol, a white, crystalline precipitate was deposited which, after crystallisation from methyl alcohol, melted at 108—110° and consisted of unchanged methylcryptopine (γ), the amount being 0·3 gram. It is curious that, in spite of the very large excess of semicarbazide employed, part of this base should have remained unchanged.

Acetylmethylcryptopine (γ).—In preparing this substance, methylcryptopine (γ) (3 grams), dissolved in freshly distilled acetic anhydride (10 c.c.), was heated in a fractionating flask just to boiling for fifteen minutes, when the liquid, which was at first colourless, soon became orange-red and then reddish-brown; the flask was then connected with the pump and the excess of acetic anhydride distilled away from the steam-bath.

The reddish-brown residue was soluble in a large excess of dilute hydrochloric acid and the clear solution soon began to deposit the sparingly soluble hydrochloride of the acetyl derivative, and the whole ultimately became a paste. The hydrochloride was collected,

washed with dilute hydrochloric acid, in which it is very sparingly soluble, and recrystallised three times from very dilute hydrochloric acid, when it was obtained as a glistening, silvery mass, very like the "silver salt" of the alizarin manufacturer, and, when quite colourless, it has a pale lilac fluorescence. In order to obtain the free acetyl derivative, the hydrochloride was dissolved in water and mixed with a slight excess of dilute ammonia, when a caseous precipitate separated which soon hardened. This was dissolved in ether, the ethereal solution dried over potassium carbonate and evaporated, when a colourless gum was obtained, which solidified completely to a striated mass melting at about 90—92° to a colourless syrup. For analysis, the substance was recrystallised from methyl alcohol:

0·1126 gave 0·2786 CO_2 and 0·0644 H_2O. C = 67·5; H = 6·3.
0·2415 „ 7·6 c.c. N_2 at 18° and 760 mm. N = 3·6.
$C_{24}H_{27}O_6N$ requires C = 67·8; H = 6·3; N = 3·3 per cent.

Acetylmethylcryptopine (γ) melts at 94—95° to a colourless syrup and is readily soluble in boiling methyl alcohol, but much less so in the cold, and separates in groups of short, well-developed prisms.

It is also readily soluble in benzene, and the addition of light petroleum and vigorous stirring causes the substance to separate almost completely as a meal of small prisms. The solution in a few drops of acetic acid gives, on the addition of sulphuric acid, a yellowish-green coloration. The *hydrochloride*, obtained as described above, melts rather sharply at 205—206° and decomposes a few degrees higher to an orange liquid with evolution of gas; on long keeping, in contact with air, it has a tendency to become violet:

0·2122 gave 0·0641 AgCl. Cl = 7·4.
$C_{24}H_{27}O_6N,HCl$ requires Cl = 7·7 per cent.

The Hydriodide.—This salt was prepared by adding potassium iodide to the hot dilute solution of the hydrochloride, when the clear liquid, on keeping, deposited brilliant, glistening scales. The salt was collected and recrystallised from water and, after drying in the steam-oven, melted at 184° with vigorous evolution of gas to a dark brown syrup:

0·1091 gave 0·2092 CO_2 and 0·0502 H_2O. C = 52·3; H = 5·1.
$C_{24}H_{27}O_6N,HI$ requires C = 52·1; H = 5·1 per cent.

This hydriodide is readily soluble in hot methyl alcohol, and separates on cooling in flat, four-sided plates with truncated edges.

The *platinichloride* is obtained, on the addition of platinic

chloride to the warm solution of the hydrochloride, as a pale yellow, chalky precipitate:

0·1174 gave 0·1964 CO_2 and 0·0498 H_2O. C = 45·6; H = 4·7.

0·2859 „ 0·0437 Pt. Pt = 15·3.

$(C_{24}H_{27}O_6N)_2,H_2PtCl_6$ requires C = 45·7; H = 4·4; N = 15·5 per cent.

Hydrolysis of the Acetyl Derivative.—In this experiment the pure acetyl derivative was digested with excess of methyl-alcoholic potassium hydroxide for ten minutes, water was then added, the viscid precipitate dissolved in ether, washed thoroughly with water, dried over potassium carbonate, and concentrated, when colourless prisms immediately commenced to separate which melted at 110—111° and consisted of methylcryptopine (γ).

Oxidation of Methylcryptopine (γ).—In this interesting oxidation, the base (5 grams), dissolved in acetone (200 c.c.), was cooled to −10°, and then oxidised by the gradual addition of very finely powdered permanganate, carbon dioxide being passed during the operation. When 6 grams had been added, the colour remained permanent for several minutes, and, after remaining overnight, the precipitate was collected and thoroughly washed with acetone. The black precipitate was extracted with much warm water and the dark brown solution acidified, when a large amount of a pale ochreous, amorphous precipitate separated, which was collected, washed thoroughly, and left in contact with porous porcelain until dry. This acid, which could not be obtained in a crystalline condition, is precipitated from its solution in methyl alcohol by ether as a chalky mass, and when this precipitation was carried out fractionally into five parts, the three middle fractions gave C = 59·8, 60·1, 59·7; H = 4·9, 5·0, 5·0; N = 2·5, 2·9, 2·8, whereas $C_{22}H_{21}O_9N$ requires C = 59·6; H = 4·7; N = 3·1 per cent., but there is no further evidence as to the nature of this acid, which is the main product of the oxidation of methylcryptopine (γ).

The aqueous mother liquor of the amorphous acid was concentrated considerably by distillation under diminished pressure and allowed to remain in the ice-chest for several days, when a granular, crystalline crust separated which was collected, dried, and recrystallised from methyl ethyl ketone, in which it is sparingly soluble, and from which it separates in crusts or needles:

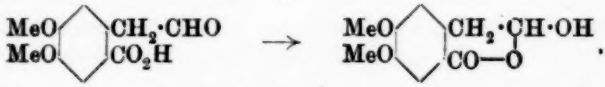
0·1166 gave 0·2519 CO_2 and 0·0568 H_2O. C = 58·9; H = 5·4.

$C_{11}H_{12}O_5$ requires C = 58·9; H = 5·3 per cent.

Methoxy-determination: 0·2704 gave 0·5636 AgI, corresponding with MeO = 27·4, whereas a substance, $C_{11}H_{12}O_5$, containing 2MeO requires MeO = 27·7 per cent. *Titration:* When the substance (0·2815) was dissolved in water, mixed with a trace of phenolphthalein, and a drop of *N*/10-sodium hydroxide added, a pink

colour was immediately obtained. Excess of $N/10$-sodium hydroxide was now added and, after boiling for five minutes, the excess was determined by titration with $N/10$-sulphuric acid, when it was found that 12·9 c.c. had been neutralised. On the assumption that the substance $C_{11}H_{12}O_5$ had been hydrolysed to a monobasic acid during the experiment, the amount of $N/10$-sodium hydroxide which should have been neutralised is 12·6 c.c.

This experiment seems to indicate that the substance $C_{11}H_{12}O_5$ is a lactone, and this view is confirmed by the fact that it is insoluble in cold dilute sodium carbonate, but dissolves in warm dilute potassium hydroxide, and the solution, on acidifying and boiling, gradually deposits the lactone. There can be little doubt that the acid produced by the hydrolysis of the lactone is 4 : 5-*dimethoxyphenylacetaldehyde*-2-*carboxylic acid*, and that this acid is incapable of existence in the free state and rapidly passes into the lactone:

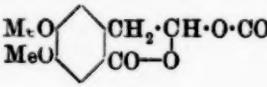


The lactone, $C_{11}H_{12}O_5$, which does not appear to have been previously described, melts at 175° and is sparingly soluble in cold, but readily so in boiling, water, and separates on cooling in microscopic groups of needles; the aqueous solution reacts almost neutral to litmus.

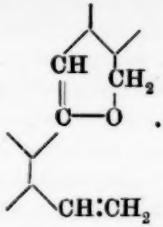
The Acetyl Derivative.—When the lactone, $C_{11}H_{12}O_5$, is mixed with freshly distilled acetic anhydride it does not dissolve in the cold, but, on warming, a clear solution is rapidly produced. After heating to boiling for ten minutes, most of the acetic anhydride was distilled off and an equal volume of glacial acetic acid added, when the acetyl derivative immediately began to separate. This was collected and recrystallised from a mixture of glacial acetic acid and acetic anhydride:

0·0955 gave 0·2048 CO_2 and 0·0469 H_2O. C = 58·5; H = 5·4.
$C_{13}H_{14}O_6$ requires C = 58·6; H = 5·3 per cent.

This *acetyl* derivative melts at 150° and is sparingly soluble in cold methyl alcohol, but dissolves readily on boiling, and crystallises well in groups of needles. Its constitution is doubtless that represented by the formula:



Anhydrocryptopidiol,



This substance is produced when the methosulphate of methylcryptopine (β) or (γ) is digested with methyl-alcoholic potassium hydroxide, and in order to obtain satisfactory results the methosulphates, and especially that of methylcryptopine (γ), should be prepared immediately before the experiment. In the first experiment the pure methosulphate of methylcryptopine (β) (2 grams) was dissolved in just sufficient boiling methyl alcohol, mixed with methyl-alcoholic potassium hydroxide (12 c.c. of 25 per cent.), and heated on the steam-bath, when the odour of trimethylamine became at once noticeable. After fifteen minutes, the bulk of the methyl alcohol was evaporated and the cloudy, yellow residue mixed with much water, when an almost colourless, chalky precipitate separated which was collected, washed well with water and dilute hydrochloric acid, and dried on porous porcelain in a desiccator.

A further considerable quantity was obtained by diluting the methyl-alcoholic mother liquors with water, when the milky liquid gradually deposited a chalky precipitate.

In order to purify this crude product, it was digested with methyl alcohol, which dissolved about 90 per cent., leaving a solid residue consisting of crude cryptopidiol (p. 974), and, after filtering, the concentrated filtrate deposited, on keeping, a flocculent precipitate:

0·1291 gave 0·3344 CO_2 and 0·0622 H_2O. C = 70·6; H = 5·4.

$C_{20}H_{18}O_5$ requires C = 71·0; H = 5·3 per cent.

Anhydrocryptopidiol melts at about 107—109° and is readily soluble in chloroform, acetone, or boiling benzene, but sparingly so in alcohol or cold benzene, and is almost insoluble in light petroleum; it is precipitated from the solution in hot benzene by light petroleum as a flocculent mass which is apparently crystalline.

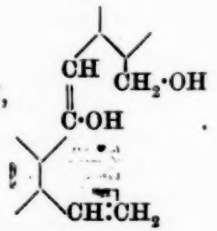
The solution in a few drops of acetic acid gives, with sulphuric acid, a violet coloration with a green tinge and, on keeping, and especially on the addition of a few drops of water, the colour changes to port-wine and the green tinge disappears. When, however, a few drops of sulphuric acid are added to the solution of the substance in much acetic acid and the test-tube is placed in

hot water, a deep crimson solution is produced and the colour is not destroyed by the addition of water.

In the second experiment, methylcryptopine (γ), which had been several times recrystallised from ether and melted at 110—111°, was converted into the methosulphate in the manner described on p. 967, and this was digested with methyl-alcoholic potassium hydroxide under the same conditions as in the case of the modification (β), except that provision was made for collecting the trimethylamine in dilute hydrochloric acid.

The acid solution was concentrated, mixed with platinic chloride, and the characteristic prisms of trimethylamine platinichloride which gradually separated were analysed. (Found, Pt=37·1. $(NMe_3)_2H_2PtCl_6$ requires Pt=37·0 per cent.) The residue in the reaction flask gave, on dilution with water, a chalky precipitate which was digested with methyl alcohol, and thus separated into a small quantity of cryptopidiol and a flocculent, readily soluble precipitate. This precipitate melted at 107—109° and had exactly similar properties, and showed the same colour reactions as the anhydrocryptopidiol obtained from methylcryptopine (β), and the identity was confirmed by analysis. (Found, C=70·5; H=5·3. $C_{20}H_{18}O_5$ requires C=71·0; H=5·3 per cent.)

Cryptopidiol,



It has already been mentioned that this substance is produced in small quantity during the action of methyl-alcoholic potassium hydroxide on the methosulphates of methylcryptopine (β) or (γ). It is remarkable that, on one occasion, the product consisted almost entirely of this substance, and the conditions employed in this particular experiment were the following: The methosulphate of methylcryptopine (γ) (2 grams) was thoroughly mixed with methyl-alcoholic potassium hydroxide (25 c.c. of 30 per cent.) and heated first on the steam-bath for an hour and then in an oil-bath at 130° until almost dry. When the viscid product was mixed with water, an ochreous mass separated which, after thoroughly washing and drying on porous porcelain over sulphuric acid, was almost insoluble in boiling methyl alcohol. The finely powdered substance was extracted in a Soxhlet apparatus with methyl alcohol for two days,

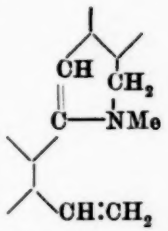
during which a substance separated from the extract in pale ochreous flakes (I), and this and the residue in the Soxhlet thimble (II) gave almost the same results on analysis:

(I) 0·1492 gave 0·3710 CO_2 and 0·0758 H_2O. C=67·8; H=5·6.
(II) 0·1319 „ 0·3245 CO_2 „ 0·0647 H_2O. C=67·0; H=5·4.
$C_{20}H_{20}O_6$ requires C=67·4; H=5·6 per cent.

Cryptopidiol is extremely stable, scarcely darkens at 250°, and does not melt until a very high temperature. It is very sparingly soluble in the usual organic solvents, but dissolves somewhat in boiling chloroform; even boiling acetic acid or acetic anhydride have very slight solvent action on this substance.

Section VIII.

Anhydrocryptopine, $C_{21}H_{21}O_4N$,



This substance was first obtained by the action of methyl-alcoholic potassium hydroxide on *iso*cryptopine sulphate under the following conditions: The sulphate (3 grams) was warmed with just enough methyl alcohol to dissolve it, methyl-alcoholic potassium hydroxide (10 c.c. of 25 per cent.) was then added, and the whole vigorously boiled on the steam-bath for fifteen minutes. The addition of water to the cold, deep yellow, cloudy mass caused the separation of a yellow, crystalline precipitate of crude anhydrocryptopine, which was collected, thoroughly washed, and rapidly* crystallised from methyl alcohol, in which it is very sparingly soluble, and from which it separates in brilliant, lemon-yellow prisms:

0·1524 gave 0·3998 CO_2 and 0·0838 H_2O. C=71·5; H=6·1.
0·4916 „ 17·2 c.c. N_2 at 19° and 756 mm. N=4·0.
$C_{21}H_{21}O_4N$ requires C=71·8; H=6·0; N=4·0 per cent.

Subsequently it was found that anhydrocryptopine is more readily obtained, and in better yield, by the following method: *iso*Cryptopine chloride, obtained by the action of phosphoryl chloride on cryptopine (compare p. 883), in quantities of 5 grams is ground, passed through a rather fine sieve, and then mixed in a flask with 20 c.c. of 25 per cent. methyl-alcoholic potassium hydr-

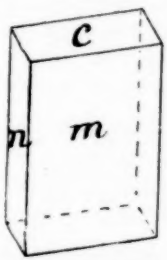
* Unless this operation is rapidly carried out, considerable loss may occur owing to the formation of methoxyanhydrocryptopine (compare p. 990).

oxide and heated to boiling on the steam-bath, when a sulphur-yellow substance separates almost immediately.

After heating for half an hour, the precipitate is collected and washed two or three times with small quantities of cold methyl alcohol,* which removes the dark impurity almost entirely, but dissolves very little of the anhydrocryptopine. The residue is then ground with water, filtered, well washed with water, and drained on porous porcelain. In this condition, anhydrocryptopine melts at 105—108°, and is quite pure enough for most experiments; for analysis it was crystallised from methyl alcohol. (Found, C=71·7; H=6·0; N=4·0. $C_{21}H_{21}O_4N$ requires C=71·8; H=6·0; N=4·0 per cent.)

Anhydrocryptopine melts at 110—111° and is usually obtained in brilliant yellow prisms, but it is, in reality, colourless or very faint lemon-yellow. It is readily soluble in boiling alcohol, acetone,

FIG. 6.



Anhydrocryptopine.

acetic ester, or benzene, but sparingly so in light petroleum. The solution of a trace of the substance in a few drops of acetic acid gives, on the addition of sulphuric acid, an orange solution with a green fluorescence and, on keeping, the colour of the solution gradually becomes deep green and still deeper on the addition of a little water.

Miss Porter finds that the substance is unsuitable for a detailed crystallographic examination. The crystals have the form of the general parallelopiped shown in Fig. 6, the measures angles being

* The methyl alcohol used in the preparation, and especially in the purification, of anhydrocryptopine must be free from acetone. If acetone is present to the extent of only one per cent., the slightly alkaline anhydrocryptopine extracts it from the methyl alcohol and combines with it, yielding a compound—presumably similar in composition to acetone berberine—which has not been obtained pure. The presence of acetone is then observed in carrying out reactions with such anhydrocryptopine as, for example, on heating with methyl sulphate, when it is disengaged.

approximately $mn = 115°$, $cm = 87°$, and $cn = 88°$. It was impossible to decide from the optical properties whether the system is triclinic or monoclinic.

Anhydrocryptopine is a weak base, since it is precipitated when the solution in glacial acetic acid is diluted with water, and it dissolves sparingly in dilute mineral acids in the cold, but, on warming, solution takes place readily, yielding deep yellow solutions, and the hydrochloride, sulphate, and nitrate are readily soluble.

The *hydriodide* separates on the addition of potassium iodide to the hot solution of the hydrochloride as a milky precipitate which, on boiling and vigorously stirring, rapidly becomes crystalline. It was collected, washed thoroughly with warm water, dried in the steam-oven, and analysed:

0·1061 gave 0·2047 CO_2 and 0·0452 H_2O. C = 52·5; H = 4·7.
$C_{21}H_{21}O_4N,HI$ requires C = 52·6; H = 4·6 per cent.

Anhydrocryptopine hydriodide is a bright yellow salt which becomes deep yellow at 170°, darkens considerably as the temperature rises, and melts at about 195°, without effervescence, to a reddish-brown gum. It is comparatively readily soluble in boiling water and, on cooling, the solution clouds and deposits an oil which, when stirred, soon crystallises. The *platinichloride* is obtained as a yellow, crystalline precipitate when platinic chloride is added to the warm solution of the hydrochloride, and becomes brown and decomposes when it is boiled with water. It was rapidly collected, washed well, and dried at 50°:

0·1551 gave 0·2564 CO_2 and 0·0561 H_2O. C = 45·1; H = 4·0.
0·5024 „ 0·0896 Pt. Pt = 17·8.
$(C_{21}H_{21}O_4N)_2,H_2PtCl_6$ requires C = 45·3; H = 4·0; Pt = 17·6 per cent.

The addition of mercuric chloride to the cold dilute solution of the hydrochloride gives a very insoluble, caseous precipitate which soon becomes crystalline. When anhydrocryptopine is boiled with 20 per cent. sulphuric acid or with concentrated hydrochloric acid, intense carmine solutions are produced and, on cooling, the corresponding salts of *epi*cryptopine separate (compare p. 1008). The action of dilute hydrochloric and sulphuric acids on anhydrocryptopine is described on pp. 994 and 1001.

Anhydrocryptopine combines with diazonium salts, as is shown by the fact that the yellow solution of the base in dilute acetic acid (40 per cent.) gives with benzenediazonium chloride a deep red coloration and, on keeping, a reddish-brown precipitate separates. Other diazonium salts behave similarly, the colour of the solution varying somewhat, but being usually intense reddish-brown. Anhydrocryptopine also shows a characteristic reaction with nitrous

acid. When dilute sodium nitrite is added at −10° to the dilute solution of the hydrochloride of the base, a rather viscid, orange precipitate separates which, on keeping and rubbing, becomes chalky. After collecting, washing with dilute hydrochloric acid, and draining on porous porcelain, the substance is a brick-red, amorphous powder, which gives an intense crimson coloration when its solution in acetic acid is mixed with sulphuric acid. The solution in phenol–sulphuric acid is also deep crimson, but does not become green when diluted with water and rendered alkaline with sodium hydroxide.

Anhydrocryptopine Methosulphate, $C_{21}H_{21}O_4N,Me_2SO_4$.

In order to prepare this substance, finely powdered anhydrocryptopine (5 grams) is mixed with methyl sulphate (5 c.c.) and heated on the steam-bath, when the mixture first liquefies to a yellow syrup, froths up and gives off a small amount of an inflammable gas, which is possibly methane, but crystallisation soon commences, and ultimately the whole sets to a bright yellow mass. This is dissolved in methyl alcohol, the solution concentrated considerably, and left in the ice-chest, when the methosulphate gradually separates in colourless, flat needles or crusts of pale amber prisms.

After collecting and washing with methyl alcohol, the substance was dissolved in boiling water, in which it is readily soluble, and the colourless, crystalline mass which separated on cooling was collected, washed with water, recrystallised until the aqueous solution gave no turbidity on the addition of dilute ammonia, and dried in the steam-oven.* Owing to its remarkable properties (see p. 852), a complete analysis of the substance was made:

0·1177 gave 0·2500 CO_2 and 0·0635 H_2O. C = 57·9; H = 6·0.
0·3868 „ 11·3 c.c. N_2 at 16·5° and 745 mm. N = 3·3.
0·2729 „ 0·1397 $BaSO_4$. S = 6·9.

$C_{21}H_{21}O_4N,Me_2SO_4$ requires C = 57·8; H = 5·7; N = 2·9; S = 6·7 per cent.

Anhydrocryptopine methosulphate begins to darken at 225—227°

* The yield from a number of experiments with varying quantities did not exceed 40 per cent. of that theoretically possible. The methyl alcohol mother liquor from the first crystallisation contains much anhydrocryptopine as sulphate or methyl hydrogen sulphate mixed with resinous matter. The addition of two volumes of water produces no precipitate, but the solution, heated at 50° and made alkaline with ammonia, gives, on keeping, a considerable chalky precipitate of crude anhydrocryptopine.

and decomposes with effervescence at about 237—238° to an orange syrup; it separates from water, in which it is sparingly soluble in the cold, in splendid, pale yellow, glistening prisms. Its solution in water is intensely bitter, and gives no precipitate on the addition of ammonia or dilute sodium hydroxide. A trace of the substance moistened with acetic acid yields, on the addition of sulphuric acid, a deep carmine solution, which soon becomes intense permanganate colour and, on boiling with water, the colour changes to a dirty green.

Action of Methyl-alcoholic Potassium Hydroxide on Anhydrocryptopine Methosulphate.

This curious conversion of anhydrocryptopine methosulphate into anhydrocryptopine is discussed on p. 852, and was carried out under the following conditions. The methosulphate, which had been crystallised twice from methyl alcohol and three times from water (2 grams), was dissolved in the least possible quantity of boiling methyl alcohol, mixed with methyl-alcoholic potassium hydroxide (8 c.c. of 25 per cent.), and boiled vigorously in an open flask in a salt-bath for about twenty minutes and in such a way that most of the methyl alcohol gradually evaporated. The pasty, almost colourless residue was mixed with water and ice, when a caseous precipitate separated which soon hardened and, after collecting, washing well, and drying on porous porcelain, the substance was sparingly soluble in methyl alcohol, and separated from the boiling solution in brilliant, almost colourless, four-sided prisms:

0·1077 gave 0·2834 CO_2 and 0·0585 H_2O. C = 71·8; H = 6·0.
$C_{21}H_{21}O_4N$ requires C = 71·8; H = 6·0 per cent.

That this substance was *anhydrocryptopine* was shown by the melting point (108—110°), by the fact that the admixture with a very pure specimen of anhydrocryptopine melted at the same temperature, and by the careful comparison of the other properties of the two preparations. As this conversion of the methosulphate into anhydrocryptopine is so unusual, involving as it does the removal of a methyl group from the nitrogen atom, the experiment was repeated three times with different preparations, but in each case with exactly the same result.

Anhydrocryptopine Methiodide, $C_{21}H_{21}O_4N$,MeI.—This substance was prepared in two different ways, namely, (i) from the methosulphate by the action of potassium iodide, and (ii) by the direct addition of methyl iodide to anhydrocryptopine.

(i) The addition of potassium iodide to the hot aqueous solution of the methosulphate produces a milky liquid and, on stirring, an almost colourless, crystalline precipitate soon forms which is somewhat soluble in hot water and separates, on cooling, in well-defined, microscopic prisms:

0·1097 gave 0·2148 CO_2 and 0·0514 H_2O. C = 53·6; H = 5·2.
$C_{21}H_{21}O_4N$,MeI requires C = 53·5; H = 5·0 per cent.

This methiodide does not darken much below 170°, becomes orange a few degrees above this, and melts and decomposes at 188—192° with much effervescence to a reddish-brown froth. It is sparingly soluble in boiling methyl alcohol, and separates, on cooling, as a pale lemon-yellow crust of prisms. It dissolves in much boiling acetone, and separates, on concentrating and leaving, in thick, yellow prisms.

(ii) *Action of Methyl Iodide on Anhydrocryptopine.*—When anhydrocryptopine (1 gram) is mixed with methyl iodide (2 grams) it dissolves and, on heating in a reflux apparatus, the additive product gradually separates and, after two or three hours, the whole is a viscid mass of crystals. This was collected and dissolved in boiling methyl alcohol, in which it was rather readily soluble, and from which a crust of nodules gradually separated. After twice recrystallising from methyl alcohol the substance was obtained in pale yellow prisms which melted and decomposed at 188—190° and consisted of anhydrocryptopine methiodide. (Found, C = 53·4; H = 5·0. $C_{21}H_{21}O_4N$,MeI requires C = 53·5; H = 5·0 per cent.)

The methyl-alcoholic mother liquor from this methiodide was concentrated considerably and, on keeping in the ice-chest, became a pasty, crystalline mass which was collected, washed with a little methyl alcohol, and left in contact with excess of dilute ammonia for twenty-four hours. By this means the hydriodide of anhydrocryptopine, which is present in considerable quantity, is decomposed, whereas the methiodides of anhydrocryptopine and methylanhydrocryptopine (compare p. 981) remain unchanged. The precipitate is collected, dried, and extracted with small quantities of boiling methyl alcohol, which dissolves the anhydrocryptopine, and this substance separates from the solution in lemon-yellow prisms melting at 110—111°. The residual mixed methiodides were several times recrystallised from methyl alcohol, and thus separated into anhydrocryptopine methiodide and a very sparingly soluble methiodide crystallising in well-defined, sulphur-yellow prisms, which begin to darken at 185°, shrink together at about 190—195°, and gradually decompose. The analysis of this substance, which becomes

opaque on drying at 100°, indicates that it is the *methiodide* of *methylanhydrocryptopine* *:

0·1085 gave 0·2168 CO_2 and 0·0519 H_2O. C = 54·5; H = 5·3.
0·2112 „ 0·0964 AgI. I = 25·7.
$C_{22}H_{23}O_4N,CH_3I$ requires C = 54·4; H = 5·1; I = 25·0 per cent.

In order to obtain the *platinichloride*, the iodide was digested with water and excess of silver chloride, and the filtered solution precipitated by platinic chloride, when a very sparingly soluble, ochreous salt was obtained:

0·1118 gave 0·0185 Pt. Pt = 16·5.
$(C_{23}H_{26}O_4N)_2PtCl_6$ requires Pt = 16·6 per cent.

When the methiodide of methylanhydrocryptopine was digested with methyl-alcoholic potassium hydroxide, decomposition took place readily, and ether extracted a yellow gum, which gradually crystallised and probably consisted of methylanhydrocryptopine, but the quantity available was unfortunately so small that further examination was out of the question.

Anhydrocryptopine Methochloride.—A very pure specimen of anhydrocryptopine methiodide was digested with water and silver chloride, and the filtered solution evaporated under diminished pressure to a small bulk, when the syrup soon crystallised. After contact with porous porcelain, the mass was twice crystallised from methyl alcohol, in which it is readily soluble, and from which it separates in brilliant, lemon-yellow prisms:

0·1031 gave 0·2475 CO_2 and 0·0571 H_2O. C = 65·5; H = 6·1.
$C_{22}H_{24}O_4NCl$ requires C = 65·7; H = 6·0 per cent.

Anhydrocryptopine methochloride melts at about 223—225° with vigorous effervescence; it is very readily soluble in water from the concentrated solution, in which it is slowly deposited in colourless crusts. The aqueous solution gives no precipitate on the addition either of dilute ammonia or sodium hydroxide, and reduces permanganate instantly at 0°. A trace of the methochloride, dis-

* Substances of this type might quite well result from the substitution of the reactive hydrogen of the =CH–, group in anhydrocryptopine according to the scheme

(compare also the probable formation of ethylanhydrocryptopine ethiodide from anhydrocryptopine and ethyl iodide, p. 983).

solved in a drop of acetic acid, gives with sulphuric acid an intense permanganate coloration. The platinichloride was obtained as a very pale, chalky precipitate on the addition of platinic chloride to the solution of the methosulphate in dilute hydrochloric acid:

0·1174 gave 0·1989 CO_2 and 0·0454 H_2O. C = 46·1; H = 4·3.

$(C_{22}H_{24}O_4N)_2PtCl_6$ requires C = 46·3; H = 4·1 per cent.

This platinichloride becomes brick-red at 200°, rapidly darkens and melts at 210—212° with effervescence to a reddish-brown mass. It is almost insoluble in water or alcohol, even at the boiling temperature. Like the corresponding methosulphate, anhydrocryptopine methochloride yields anhydrocryptopine when it is decomposed by alkalis. In this experiment the pure substance (2 grams) was digested with methyl alcoholic potassium hydroxide (5 c.c. of 25 per cent.) for five minutes, the product mixed with water, and the caseous precipitate extracted with ether. After washing thoroughly and drying over potassium carbonate, the ethereal solution deposited, on evaporation, a syrup which soon crystallised, and rubbing with a little methyl alcohol dissolved resinous impurity and left a crystalline mass which separated from methyl alcohol in yellow prisms, melted at 107—109°, and consisted of anhydrocryptopine.

When the methochloride of anhydrocryptopine is boiled with concentrated hydrochloric acid for five minutes, the excess of hydrochloric acid distilled off, and, after dissolving in a little water, the solution left in the ice-chest, a crystalline crust separates which decomposes at about 120—125° to a yellow froth. The solution of this chloride in acetic acid gave, on the addition of sulphuric acid, an intense bluish-violet coloration which soon became redder and ultimately permanganate colour, and the aqueous solution of the chloride is coloured crimson by nitric acid. It is obvious that this chloride is identical with ψ-cryptopine chloride, which was subsequently prepared in quantity from anhydrocryptopine methosulphate by the action of concentrated hydrochloric acid (p. 984), and this was confirmed by analysis. (Found, C = 64·5; H = 5·9. $C_{21}H_{22}O_4NCl$ requires C = 65·0; H = 5·7 per cent.)

Anhydrocryptopine Ethiodide, $C_{21}H_{21}O_4N$,EtI.—Anhydrocryptopine dissolves readily in, but exhibits little tendency to combine with, ethyl iodide, and when the solution is heated, complex changes occur, much tar is formed, and only traces of crystalline substance can be extracted by treatment with water, alcohol, or other solvents. The best results were obtained by leaving the solution of anhydrocryptopine in three times its weight of ethyl iodide at the ordinary temperature for several days, when a small, crystalline crust separated which crystallised from alcohol, in which it was remarkably

sparingly soluble, in orange-red nodules. This substance melted at 228—230° with effervescence, and evidently consisted of anhydrocryptopine ethiodide, but the yield was very small:

0·1071 gave 0·2130 CO_2 and 0·0469 H_2O. C=54·2; H=4·9.

$C_{21}H_{21}O_4N,C_2H_5I$ requires C=54·4; H=5·1 per cent.

During the recrystallisation of this ethiodide, a very sparingly soluble substance separated in crimson needles, which melted at 290—295° to a black froth and was somewhat soluble in boiling water, yielding a yellow solution which gave no precipitate with ammonia, but an immediate milkiness on the addition of concentrated aqueous sodium hydroxide. The analysis indicates that this substance is probably the ethiodide of ethylanhydrocryptopine, corresponding with the methiodide obtained as one of the products of the action of methyl iodide on anhydrocryptopine (compare p. 981):

0·1107 gave 0·2266 CO_2 and 0·0521 H_2O. C=55·8; H=5·2.

$C_{23}H_{25}O_4N,C_2H_5I$ requires C=56·0; H=5·6 per cent.

Action of Ethyl Sulphate on Anhydrocryptopine.—The behaviour of anhydrocryptopine with pure ethyl sulphate was investigated under a variety of conditions, but in no case could any crystalline additive product be isolated. The base (1 gram) dissolves readily in warm ethyl sulphate (1·5 c.c.) and, on heating on the steam-bath, the liquid becomes deep brown and finally black, and no crystals separate from the tarry product on keeping. A definite and curious result was, however, obtained when anhydrocryptopine and ethyl sulphate, in the proportions stated above, were dissolved in benzene (10 c.c.) and left for six weeks in a loosely-corked flask. The dark brown benzene solution was decanted from a brown, viscid mass which had been gradually deposited, and this was warmed with water, when a considerable amount of solid separated. This was collected, rubbed with methyl alcohol, and the sparingly soluble, yellow, crystalline mass again collected and recrystallised twice from methyl alcohol, from which it separated in colourless balls of needles. This substance weighed 0·24 gram, melted at 163°, and consisted of ketoanhydrocryptopine (Found, C=68·7; H=5·2. $C_{21}H_{19}O_5N$ requires C=69·1; H=5·2 per cent.), but the examination of the mother liquors gave no clue to the reasons for the formation of this substance, which must have been produced by the oxidation of the anhydrocryptopine or of some derivative (compare p. 986).

Action of Concentrated Hydrochloric Acid on Anhydrocryptopine Methosulphate. Formation of ψ-Cryptopine Chloride.

Anhydrocryptopine methosulphate (2 grams) dissolves readily in concentrated hydrochloric acid (5 c.c.) and, if the solution is gently boiled for ten minutes by means of a sulphuric acid-bath and the hydrochloric acid then distilled off, a pale yellow syrup remains which sets to a pasty mass on mixing with a little water. The whole was boiled with just enough water to give a clear solution and allowed to cool slowly, when a granular precipitate separated which was collected and twice recrystallised from dilute hydrochloric acid:

0·1162 gave 0·2761 CO_2 and 0·0593 H_2O. C = 64·8; H = 5·7.

$C_{21}H_{22}O_4NCl$ requires C = 65·0; H = 5·7 per cent.

ψ-Cryptopine chloride is readily soluble in hot water, but much less so in the cold and still less so in dilute hydrochloric acid; it is also readily soluble in methyl alcohol. When heated in a capillary tube it softens and melts at about 110°, and effervesces vigorously at about 123—125° to a yellow froth, which becomes red a few degrees higher. A solution of the chloride in a very little glacial acetic acid gives, on the addition of sulphuric acid, a deep bluish-violet coloration which gradually reddens and ultimately becomes the colour of permanganate. A trace of the substance on a watch-glass is coloured an intense crimson by concentrated nitric acid and dissolves to a brown solution, and the addition of a drop of nitric acid to a dilute solution of the chloride produces a deep reddish-violet coloration which deepens and becomes redder on boiling. When the solution of the chloride in acetic acid is mixed with benzenediazonium chloride, a deep port-wine coloration is produced which remains on dilution, and the aqueous solution of the chloride also gives a deep violet coloration on the addition of benzenediazonium chloride. The aqueous solution of ψ-cryptopine chloride decolorises permanganate instantly even at 0°.

ψ-Cryptopine Iodide, $C_{21}H_{22}O_4NI$.—When potassium iodide is added to a moderately concentrated aqueous solution of the chloride, a heavy, white precipitate is immediately produced, but if a boiling, very dilute solution of the chloride is mixed with boiling dilute potassium iodide, a clear solution is obtained, which almost immediately begins to deposit a glistening mass of scales:

0·1070 gave 0·2069 CO_2 and 0·0490 H_2O. C = 52·7; H = 5·0.

$C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·6 per cent.

ψ-Cryptopine iodide gradually darkens above 160°, and melts and decomposes at 232—235° with vigorous effervescence to a reddish-brown froth. It is very sparingly soluble in water and dissolves

sparingly in boiling alcohol, from which it separates as a microscopic mass of glistening prisms consisting of rhombs and six-sided plates.

The *platinichloride* separates as an ochreous precipitate on the addition of platinic chloride to the hot solution of the chloride in very dilute hydrochloric acid, and the mother liquor is pink:

0·1092 gave 0·1825 CO_2 and 0·0422 H_2O. C = 45·5; H = 4·3.

0·2125 „ 0·0368 Pt. Pt = 17·3.

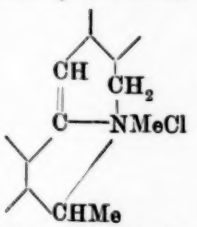
$(C_{21}H_{22}O_4N)_2PtCl_6$ requires C = 45·3; H = 4·0; Pt = 17·5 per cent.

The aqueous solution of ψ-cryptopine chloride is coloured yellow by the addition of dilute ammonia, but no precipitate forms. When a warm concentrated solution is mixed with 10 per cent. sodium hydroxide, a cloudy liquid is produced, and a crystalline precipitate soon separates, which is evidently the unchanged chloride, since the addition of hot water produces a clear solution, and this behaviour characterises the chloride as a quaternary salt. When, however, the solution in warm dilute sodium hydroxide is boiled, decomposition sets in, the liquid darkens, becomes greenish-brown, and a blue precipitate separates which is insoluble in water. The solution of the chloride in methyl alcohol gives, on the addition of methyl-alcoholic potassium hydroxide (25 per cent.), a cloudy liquid which, when warmed at 45°, becomes first reddish-brown, then intense violet, green, and finally almost black. If the product is now diluted with water, a nearly black base separates, which dissolves in dilute hydrochloric acid to an intense reddish-brown solution, and in many respects resembles dehydro*epi*cryptopirubin hydroxide (p. 1017). This base was thoroughly washed, dried in the steam-oven, and analysed:

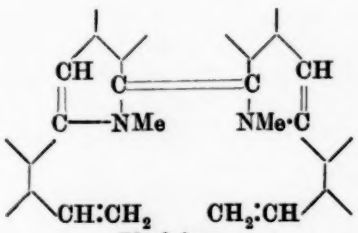
0·1011 gave 0·2662 CO_2 and 0·0504 H_2O. C = 71·7; H = 5·6.

$C_{21}H_{19}O_4N$ requires C = 72·2; H = 5·4 per cent.

It is suggested in the Introduction (p. 855) that the constitutions of ψ-cryptopine chloride and the black base are those represented by the formulæ:



ψ-Cryptopine chloride.



Black base.

Oxidation of Anhydrocryptopine.

This oxidation was carried out under the following conditions: Anhydrocryptopine (5 grams), dissolved in acetone (400 c.c.), was cooled to $-10°$, and then very finely powdered permanganate gradually added with constant shaking, when oxidation took place readily until 4 grams had been used. After remaining overnight, the whole was filtered, the manganese precipitate carefully washed with acetone, left exposed to the air until free from the solvent, and extracted with warm water. The tarry precipitate, which separated on acidifying the deep brown solution, was collected and rubbed with a little methyl alcohol, when it deposited a colourless precipitate of *norketoanhydrocryptopic acid*, which acid was subsequently obtained in larger quantity from the product of the oxidation of ketoanhydrocryptopine (p. 988). The acetone filtrate from the manganese precipitate was freed from acetone by distillation from the water-bath under diminished pressure, and the viscid, brown syrup, which partly crystallised, dissolved in warm glacial acetic acid. The deep brown solution was poured into much water, which caused partial dissociation of the acetate, and the cloudy liquid was extracted with ether, the ethereal solution well washed with dilute sodium carbonate, dried over potassium carbonate, concentrated considerably, and left in the ice-chest for several days. The ochreous, crystalline crust which had separated was collected, washed with ether, and several times recrystallised from methyl alcohol:

0·1104 gave 0·2788 CO_2 and 0·0531 H_2O. C = 68·9; H = 5·3.
0·1111 „ 0·2799 CO_2 „ 0·0538 H_2O. C = 68·8; H = 5·4.
0·4448 „ 15·5 c.c. N_2 at 18° and 761 mm. N = 4·0.

$C_{21}H_{19}O_5N$ requires C = 69·1; H = 5·2; N = 3·8 per cent.

Ketoanhydrocryptopine melts at 163° and is characterised by the facility with which it crystallises and by its remarkable stability. It is sparingly soluble in methyl alcohol, and separates in long, pale ochreous needles; it also crystallises well from benzene, in which it is sparingly soluble, and with which it readily forms supersaturated solutions, in groups of colourless, glistening, flat needles, becoming opaque in the steam-oven, and exhibiting the following curious behaviour. The dry substance softens at 145° and melts at 155° with effervescence and, warmed with methyl alcohol, it swells up to a voluminous mass. This dissolves in boiling methyl alcohol and, on cooling, a colourless mass of glistening crystals separates, which become opaque in the steam-oven and melt at 163—164°. Ketoanhydrocryptopine has only very slight basic properties, since it is insoluble in boiling dilute sulphuric or hydro-

chloric acids, and its solution in acetic acid is precipitated by water. When, however, it is boiled with concentrated hydrochloric acid, a deep yellow solution is produced, and from this a bright orange substance separates on cooling, which seems to be the hydrochloride, since water destroys the colour, and the colourless substance melting at 163° is precipitated.

It does not appear to be attacked by alkali hydroxides because, after boiling with a large excess of methyl-alcoholic potassium hydroxide for ten minutes, water precipitated the unchanged substance. Attempts to obtain a semicarbazone or oxime were unsuccessful. The solution in a few drops of acetic acid gives, on the addition of sulphuric acid, a yellow solution which exhibits a slight green fluorescence and becomes brown on the addition of water.

The brown aqueous acetic acid solution from which the keto-anhydrocryptopine had been extracted with ether, was rendered strongly alkaline by the addition of potassium hydroxide, and the yellow precipitate repeatedly extracted with ether. The ethereal solution was washed, dried over potassium carbonate, and evaporated to a small bulk when, after remaining in the ice-chest for several days, a brown, crystalline crust had separated which, when dried in the steam-oven, was an intensely orange powder and had the appearance of a quinone. It was purified by solution in glacial acetic acid and, after the addition of water, the slight milkiness was removed by ether, the aqueous solution again made alkaline, and the precipitate recrystallised from ether:

0·1228 gave 0·2947 CO_2 and 0·0613 H_2O. C = 65·4; H = 5·5.
0·1041 „ 0·2497 CO_2 „ 0·0527 H_2O. C = 65·4; H = 5·6.
0·3660 „ 11·3 c.c. N_2 at 19·5° and 765 mm. N = 3·6.

$C_{21}H_{21}O_6N$ requires C = 65·7; H = 5·5; N = 3·7 per cent.

When heated in a capillary tube this base gradually becomes deep red and decomposes at about 150°; it is readily soluble in methyl alcohol or acetone, but sparingly so in ether. When it is mixed with dilute hydrochloric acid, the orange-red colour of the base changes to a bright yellow owing to the formation of a sparingly soluble salt (probably the quaternary chloride). This dissolves in boiling water, but apparently with some dissociation, and the yellow aqueous solution is not precipitated by dilute ammonia, but gives, with sodium hydroxide, a pale yellow, gelatinous precipitate which, on warming, becomes granular and apparently crystalline. The *platinichloride* is a bright orange-yellow precipitate which, on warming, becomes chalky, and is then readily filtered:

0·3010 gave 0·0516 Pt. Pt = 17·1.

$(C_{21}H_{20}O_5N)_2PtCl_6$ requires Pt = 17·2 per cent.

The addition of mercuric chloride to the solution of the hydrochloride gives a bright yellow precipitate which is soluble in boiling water and separates in chrome-yellow flocks, and the picrate is a voluminous, bright yellow precipitate somewhat soluble in hot water.

Oxidation of Ketoanhydrocryptopine.

In this oxidation the substance (3 grams), dissolved in acetone (150 c.c.), was gradually mixed with permanganate (3 grams) at the ordinary temperature, when oxidation took place readily. After collecting and thoroughly washing with acetone, the precipitate was extracted with warm water and the brown solution acidified, when an ochreous precipitate separated, which was collected, washed with ether, and then with methyl alcohol. The acid was then dissolved in dilute sodium carbonate, and after heating with animal charcoal, mechanically stirred and fractionally precipitated with very dilute hydrochloric acid into three portions, when the middle fraction, after drying over phosphoric oxide, was analysed:

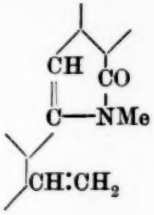
0·1087 gave 0·2497 CO_2 and 0·0455 H_2O. C = 62·6; H = 4·6.
0·2842 „ 9·5 c.c. N_2 at 18° and 760 mm. N = 3·7.
$C_{20}H_{17}O_7N$ requires C = 62·3; H = 4·9; N = 3·6 per cent.

This substance, which has been provisionally named *norketoanhydrocryptopic acid*, shrinks at about 145—150° and melts at about 165° to a resin, and exhibits little facility for crystallising, although on one occasion it separated from methyl alcohol in small needles. It dissolves readily in acetic acid and the solution gives, on the addition of sulphuric acid, a brownish-green coloration which, on adding a little water, becomes deep claret. When this acid is boiled with anhydrous formic acid, it dissolves, and a satiny, crystalline mass separates which, after collecting and washing with formic acid, is almost insoluble in the usual solvents. It was boiled with a large quantity of glacial acetic acid, in which it is remarkably sparingly soluble, and from which it separates as a grey, satiny mass of needles:

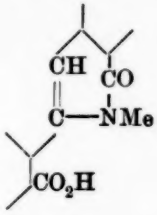
0·1155 gave 0·2784 CO_2 and 0·0454 H_2O. C = 65·7; H = 4·5.
0·2489 „ 9·6 c.c. N_2 at 20° and 761 mm. N = 3·8.
$C_{20}H_{15}O_6N$ requires C = 65·4; H = 4·6; N = 3·8 per cent.

Dehydronorketoanhydrocryptopic acid has no definite melting point and is a remarkably stable substance, which seems to be quite unaffected by boiling with dilute alkali hydroxides or acids. It is suggested in the Introduction (p. 852) that the relationship existing between ketoanhydrocryptopine (I), norketoanhydrocrypto-

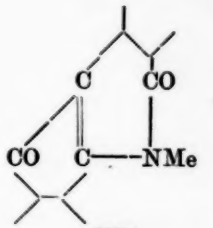
pic acid (II), and dehydronorketoanhydrocryptopic acid (III) is that represented by the formulæ:



(I).



(II.)



(III.)

Unfortunately, the difficulty in obtaining these substances in anything but very small quantities has made it impossible to examine them in greater detail.

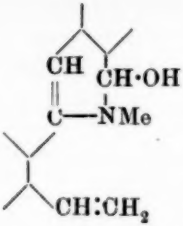
Reduction of Anhydrocryptopine to Anhydrodihydrocryptopine (B).

In this reduction, anhydrocryptopine (1 gram) was dissolved in water (30 c.c.) and sulphuric acid (0·5 c.c.) and then 50 grams of 4 per cent. sodium amalgam added all at once, the whole being maintained at about 80° and kept acid by the addition from time to time of 25 per cent. sulphuric acid. The product, which usually contains crystalline crusts of the sulphate of anhydrodihydrocryptopine, was completely dissolved in hot water, rendered alkaline with sodium hydroxide, and several times extracted with ether. After the ethereal solution had been dried over potassium carbonate, it was concentrated and left in the ice-chest, when a crust of lemon-yellow prisms gradually separated which melted at 124° and, after recrystallisation from methyl alcohol, the brilliant, almost colourless prisms became opaque in the steam-oven:

0·0992 gave 0·2596 CO_2 and 0·0590 H_2O. C = 71·4; H = 6·6.

$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.

That this substance was *anhydrodihydrocryptopine* (p. 941) was proved by careful comparison and by the fact that the admixture with a sample of this substance, which had been obtained from dihydrocryptopine, melted at 124—126°. Subsequently, this reduction was carried out on a considerably larger scale, and as the yield is at least 70 per cent. of that theoretically possible, the process is convenient, and was actually employed in the preparation of much of the anhydrodihydrocryptopine required for the investigation of that substance.

Hydroxyanhydrocryptopine,  *and its Derivatives.*

It has already been mentioned that anhydrocryptopine crystallises splendidly from methyl alcohol in pale yellow prisms, and during the purification of several different preparations in this way it was always noticed that the mother liquor, even when the pure substance had been employed and the crystallisation was rapidly carried out, had a tendency to become dark coloured. In order to investigate the cause of this, a concentrated solution of anhydrocryptopine in boiling methyl alcohol was boiled for an hour, during which it became dark brown and, on concentrating and leaving in the ice-chest for several days, brown nodules separated which, in some cases, were almost black. These were collected and recrystallised from methyl alcohol, in which the substance is very sparingly soluble, and from which it separates as a crust of pale brown or sometimes almost colourless prisms.* This substance is methoxyanhydrocryptopine (*A*), $C_{21}H_{20}(OMe)O_4N$ (compare p. 856). The following analyses (I) and (II) were made with different preparations:

* The formation of this substance has been observed under a variety of conditions. In one case, a saturated solution of anhydrocryptopine in boiling methyl alcohol contained in a beaker, deposited, on cooling, small, brilliant yellow crystals of anhydrocryptopine. When the whole was accidentally left for the week-end exposed to the air, the yellow crystals became replaced by a mass of garnet, prismatic needles of methoxyanhydrocryptopine, which melted at about 184°. The garnet colour of such crystals appears to be only superficial, since they yield an almost colourless powder when crushed.

In order to demonstrate the absorption of oxygen during the conversion of anhydrocryptopine into the methoxy-derivative, a freshly prepared, boiling, saturated solution of the base in methyl alcohol (15 c.c.) was introduced into a eudiometer tube of 150 c.c. capacity and filled with mercury. Oxygen (75 c.c.) was then passed up and although absorption was at first very slow, after twenty-four hours, 5 c.c. of gas had been taken up, the solution had become brown, and during the next twenty-four hours a further 2 c.c. of oxygen was absorbed. The change from anhydrocryptopine to the methoxy-derivative could be well observed on the walls of the eudiometer as the bright yellow crystals of the former gradually gave place to the garnet-coloured colonies of the latter.

(I) 0·1664 gave 0·4225 CO_2 and 0·0944 H_2O. C = 69·2; H = 6·2.
(II) 0·1427 „ 0·3619 CO_2 „ 0·0791 H_2O. C = 69·2; H = 6·1.
(I) 0·4033 „ 13·2 c.c. N_2 at 17·5° and 760 mm. N = 3·8.
$C_{22}H_{23}O_5N$ requires C = 69·3; H = 6·0; N = 3·7 per cent.

Methoxy-determination: 0·3356 gave 0·6045 AgI. OMe = 23·8. $C_{22}H_{23}O_5N$, containing 3MeO, requires OMe = 24·4 per cent.

Methoxyanhydrocryptopine (*A*), if rapidly heated, darkens above 160° and melts at about 186—188°, with evolution of gas, to a black mass.

It is more readily soluble in ethyl than in methyl alcohol, and separates from the latter solvent in well-developed, pale amber prisms, which may, however, be garnet-coloured if the boiling with the alcohol has been prolonged. It dissolves readily in benzene or acetic ester, and separates with difficulty as an almost colourless crust of small prisms, and all the solutions stain the skin deep yellow.

The solution of a crystal in a drop of acetic acid is deep yellow, and yields, on the addition of sulphuric acid, a pale yellow solution exhibiting a slight green fluorescence.

Like cotarnine and its alkyl derivatives, it readily yields condensation products with a variety of substances, for example, although itself very sparingly soluble in methyl alcohol, it dissolves readily on the addition of nitromethane or trinitrotoluene, yielding reddish-brown and deep brownish-violet solutions respectively.

Methoxyanhydrocryptopine (*B*).—The dark brown mother liquors from the preparation of methoxyanhydrocryptopine (*A*) yielded, when they were left exposed to air, crusts of deep brown crystals which contain small quantities of the (*A*) modification, but consist mainly of methoxyanhydrocryptopine (*B*). The latter is obtained pure, by fractional crystallisation from methyl alcohol, in amber or brown groups of thin prisms which melt at 160—162°, and the melting point is not altered by further recrystallisation. The crystals become opaque when dried in the steam-oven, whereas the (*A*) modification remains quite bright in these circumstances:

0·1658 gave 0·4214 CO_2 and 0·0939 H_2O. C = 69·2; H = 6·3.
0·3994 „ 13·1 c.c. N_2 at 18° and 756 mm. N = 3·7.
$C_{22}H_{23}O_5N$ requires C = 69·3; H = 6·0; N = 3·7 per cent.

So far as could be judged, the behaviour of this substance towards acids is exactly the same as that exhibited by the (*A*) modification, as, indeed, was to be expected.

Ethoxyanhydrocryptopine (*A*), $C_{21}H_{20}(OEt)O_4N$.—This substance was obtained by boiling anhydrocryptopine with ethyl alcohol for half an hour and then concentrating the solution when, on remain-

ing in the ice-chest, brown nodules gradually separated, but crystallisation was more sluggish than in the corresponding case of the methoxy-derivative. After recrystallisation from alcohol, from which the substance separated in pale brown crusts, the following analytical results were obtained:

0·1269 gave 0·3233 CO_2 and 0·0730 H_2O. C = 69·4; H = 6·4.

0·3006 „ 10·4 c.c. N_2 at 16° and 763 mm. N = 3·9.

$C_{23}H_{25}O_5N$ requires C = 69·9; H = 6·3; N = 3·5 per cent.

Ethoxyanhydrocryptopine (*A*) melts at about 152° with gradual decomposition, and exhibits towards reagents the same properties as do the methoxyanhydrocryptopines. Thus the solution in glacial acetic acid is deep yellow and, on the addition of sulphuric acid, there is no definite change, but the solution exhibits a slight pale green fluorescence. The mother liquors from the crystallisation of ethoxycryptopine (*A*) contain a second substance, which melts roughly at 125—130° and possibly consists of the (*B*)-isomeride, but the amount of material was, unfortunately, insufficient to allow of this substance, if present, being isolated in a pure condition.

Hydroxyanhydrocryptopine, $C_{21}H_{20}(OH)O_4N$.—This substance is obtained when either methoxy- or ethoxy-anhydrocryptopine is dissolved in dilute hydrochloric acid and the solution precipitated by the addition of concentrated alkali hydroxide. Finely divided methoxyanhydrocryptopine (*A*) dissolves readily in dilute hydrochloric acid, producing a bright orange solution, and, after remaining for several minutes, ammonia does not give a precipitate in the cold with a dilute solution of the salt. The addition of sodium hydroxide (20 per cent.) liberates the base, however, as an almost colourless, chalky precipitate which, after collecting, thoroughly washing, and drying on porous porcelain in a vacuum desiccator, gave, on analysis, numbers which agreed only approximately with the formula $C_{21}H_{21}O_5N$. The substance was therefore dissolved in pure dry ether, the ethereal solution concentrated, and left in the ice-chest, when rather indefinite, pale ochreous crusts gradually separated:

0·1116 gave 0·2816 CO_2 and 0·0580 H_2O. C = 68·8; H = 5·8.

0·3607 „ 12·6 c.c. N_2 at 15° and 762 mm. N = 3·9.

$C_{21}H_{21}O_5N$ requires C = 68·7; H = 5·7; N = 3·8 per cent.

Hydroxyanhydrocryptopine has no definite melting point; it softens at 120° and gradually decomposes, as the temperature rises, to a reddish-brown froth. It dissolves readily in the usual solvents and, when boiled with methyl alcohol and the solution concentrated, crusts of methoxyanhydrocryptopine (*A*), melting at 188—190°, gradually separate.

The Chloride, $C_{21}H_{20}O_4NCl$.—If the intense orange solution of

hydroxyanhydrocryptopine in dilute hydrochloric acid is allowed to evaporate over potassium hydroxide and sulphuric acid in a vacuum desiccator, a brown resin remains and, on rubbing this with a good deal of acetone, crystals gradually develop and the filtered acetone solution deposits balls of brilliant orange needles. For analysis, this chloride was collected, washed with acetone, in which it is sparingly soluble, and dried in the steam-oven:

0·3085 gave 0·1098 AgCl. Cl = 8·7.

$C_{21}H_{20}O_4NCl$ requires Cl = 8·9 per cent.

This chloride is rather sparingly soluble in cold water, but dissolves readily on boiling to an orange solution, which sets to a jelly when cooled, but, if a crystal is introduced into the warm solution and the whole well stirred, the chloride separates as a woolly mass of slender, orange needles. The aqueous solution gives, on the addition of potassium cyanide, a voluminous, chalky precipitate of the cyanide, which is sparingly soluble in water.

The Iodide, $C_{21}H_{20}O_4NI$.—This splendid salt was obtained, on adding potassium iodide to the solution of the chloride, as a pale orange, caseous precipitate, and was collected, thoroughly washed, dried on porous porcelain, and crystallised from methyl alcohol, in which it is moderately readily soluble, and from which it separates as a crust of brilliant, well-developed, orange prisms:

0·1207 gave 0·2346 CO_2 and 0·0472 H_2O. C = 53·0; H = 4·3.

$C_{21}H_{20}O_4NI$ requires C = 52·8; H = 4·2 per cent.

When heated in a capillary tube, this salt gradually becomes redder; at 200° it is brick-red, and melts at about 230°, with evolution of gas, to a reddish-brown mass which gradually becomes black. It is sparingly soluble in alcohol or water in the cold, but dissolves in boiling water to a pale yellow solution and separates, on cooling, as a viscid precipitate which becomes crystalline on rubbing.

The Platinichloride, $(C_{21}H_{20}O_4N)_2PtCl_6$.—This is obtained on the addition of platinic chloride to the dilute solution of the chloride, as a brilliant, chrome-yellow, caseous precipitate which becomes chalky on warming gently. It was collected, washed thoroughly, dried on porous porcelain, and then in the steam-oven:

0·1261 gave 0·2115 CO_2 and 0·0446 H_2O. C = 45·7; H = 3·9.

0·2674 „ 0·0472 Pt. Pt = 17·6.

$(C_{21}H_{20}O_4N)_2PtCl_6$ requires C = 45·5; H = 3·6; Pt = 17·6 per cent.

This platinichloride has no definite melting point; it begins to change colour at 200°, is brick-red at 215°, and nearly black at 240°.

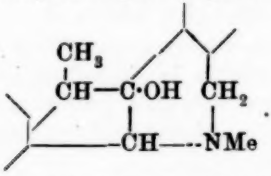
Oxidation of Hydroxyanhydrocryptopine to Ketoanhydrocryptopine.

In carrying out this experiment, hydroxyanhydrocryptopine (2·5 grams) dissolved in acetone (100 c.c.) was cooled to 0° and gradually mixed with very finely powdered potassium permanganate (2 grams), when oxidation took place rather slowly. After remaining overnight, the product was filtered, the manganese precipitate washed with acetone, and the combined acetone extracts evaporated under diminished pressure. The residual, brown syrup was dissolved in a little glacial acetic acid, mixed with much water, the milky liquid extracted with ether, the ethereal solution washed, dried over potassium carbonate, and evaporated to a small bulk when, on keeping in the ice-chest for several days, brown, nodular masses separated. In this condition, the substance melted at 145—150°, but after recrystallisation from methyl alcohol at 159—161°, and consisted of ketoanhydrocryptopine (p. 986; Found, C = 68·7; H = 5·3. $C_{21}H_{19}O_5N$ requires C = 69·1; H = 5·2 per cent.).

Since the yield of this substance was very small, the manganese precipitate was examined, but, after extraction with warm water, the pale brown solution gave, on acidifying, only a trace of an amorphous, brown acid which could not be identified.

Section IX.

The Hydroxyisoanhydrodihydrocryptopines,



It has already been stated in the Introduction (p. 860) that boiling with dilute hydrochloric acid converts anhydrocryptopine into two isomeric, colourless hydrochlorides, $C_{21}H_{23}O_5N,HCl$, which are also isomeric with cryptopine hydrochloride, and, for reasons which were then discussed, these hydrochlorides have been named the (*A*) and (*B*) *hydrochlorides* of *hydroxyisoanhydrodihydrocryptopine*. These hydrochlorides are characterised by widely differing melting points; the hydrochloride (*A*) melts at 227° and the hydrochloride (*B*) at 177°, and the best conditions of formation seem to be the following. Anhydrocryptopine (2 grams) dissolved in concentrated hydrochloric acid (2 c.c.) and water (8 c.c.) is heated on the steam-bath, when the yellow solution gradually becomes deep orange, and in half an hour crystals sometimes com-

mence to separate from the hot liquid. The product is allowed to cool slowly, and is frequently stirred, when a heavy, crystalline precipitate rapidly forms and, after remaining in the ice-chest overnight, this is collected and recrystallised from boiling water, in which it is sparingly soluble. The crystalline mass, which consists of *hydroxy*iso*anhydrodihydrocryptopine hydrochloride* (*A*), is collected, drained on porous porcelain, and dried in the steam-oven:

0·1121 gave 0·2554 CO_2 and 0·0608 H_2O. C = 62·1; H = 6·0.

$C_{21}H_{23}O_5N,HCl$ requires C = 62·1; H = 5·9 per cent.

This hydrochloride (*A*) melts and decomposes at about 227°, is very sparingly soluble in water and remarkably so in dilute hydrochloric acid, and separates from its hot aqueous solution in colourless groups of needles. It dissolves somewhat readily in boiling methyl alcohol and, if the solution is allowed to cool slowly, crystallises beautifully in stars of needles, which melt at 227° with decomposition to a yellow froth.

The *hydriodide* (*A*), $C_{21}H_{23}O_5N,HI$, is obtained, on the addition of potassium iodide to the hot dilute aqueous solution of the hydrochloride, as a viscid precipitate which melts under boiling water, but becomes crystalline on rubbing. It is comparatively readily soluble in boiling methyl alcohol, and separates in small prisms which become brick-red at 190° and decompose at 205° with effervescence to a bright-red froth:

0·1037 gave 0·1935 CO_2 and 0·0463 H_2O. C = 50·9; H = 5·0.

$C_{21}H_{23}O_5N,HI$ requires C = 51·1; H = 4·9 per cent.

The *platinichloride* (*A*), $(C_{21}H_{23}O_5N)_2,H_2PtCl_6$, separates as a pale ochreous, caseous precipitate when platinic chloride is added to the hot dilute solution of the hydrochloride. It is appreciably soluble in boiling water and separates, on cooling, as a chalky powder which darkens at 200° and decomposes, with frothing, at about 210° to a black mass:

0·1159 gave 0·1868 CO_2 and 0·0437 H_2O. C = 43·9; H = 4·3.

$(C_{21}H_{23}O_5N)_2,H_2PtCl_6$ requires C = 43·9; H = 4·2 per cent.

*Action of Nitrous Acid on Hydroxy*iso*anhydrodihydrocryptopine* (*A*).

The warm aqueous solution of the hydrochloride (*A*) (1 gram) gives, on the addition of sodium nitrite (0·6 gram), a sparingly soluble precipitate which is apparently the nitrite; this dissolves on the steam-bath, the liquid clouds, much gas is given off, and a small quantity of a brown gum separates. After heating for an hour, the product was filtered, and the yellow filtrate rendered alkaline with ammonia, causing a chalky precipitate to separate.

This was collected, dissolved in ether, the ethereal solution filtered from a small quantity of insoluble gum, concentrated, and left in the ice-chest, when a crust separated which was rather indefinite but apparently crystalline:

0·1118 gave 0·2692 CO_2 and 0·0615 H_2O. C = 65·6; H = 6·1.

0·3454 „ 12·0 c.c. N_2 at 19° and 754 mm. N = 4·0.

$C_{21}H_{23}O_6N$ requires C = 65·4; H = 6·0; N = 3·6 per cent.

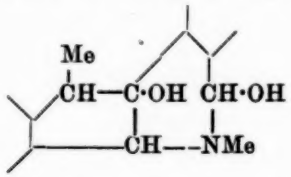
This substance is readily soluble in acetic acid, and the deep yellow solution is not precipitated by water; the solution in dilute hydrochloric acid is also orange-yellow. It is readily soluble in methyl alcohol or benzene, and is precipitated from the benzene solution by light petroleum as a colourless mass which, apparently, is not crystalline. The *platinichloride* is obtained, on the addition of platinic chloride to the warm solution of the hydrochloride, as a fine, chrome-yellow, chalky precipitate which was dried over phosphoric oxide, since it melts to a resin in the steam-oven:

0·1288 gave 0·2025 CO_2 and 0·0479 H_2O. C = 42·9; H = 4·1.

0·3628 „ 0·0613 Pt. Pt = 16·9.

$(C_{21}H_{23}O_6N)_2,H_2PtCl_6$ requires C = 42·7; H = 4·1; Pt = 16·5 per cent.

The above analyses seem to indicate that this substance is a *dihydroxy*iso*anhydrodihydrocryptopine*, and its properties, and especially the deep yellow colour of its salts, suggest that it is a hydrocotarnine derivative containing the grouping:



*Hydroxy*iso*anhydrodihydrocryptopine* (*A*).—The hydrochloride (*A*) is very sparingly soluble in cold water, but the concentrated solution in boiling water may be cooled to 25° without crystallising, provided it is not stirred. In order to obtain the base, such a solution was mixed with excess of ammonia, when a milky liquid resulted and a putty-like mass separated which soon hardened. The decanted liquid deposited a further quantity of the base as a chalky powder, and this was collected, thoroughly washed, and dried over phosphoric oxide:

0·1021 gave 0·2540 CO_2 and 0·0584 H_2O. C = 67·8; H = 6·3.

0·2405 „ 8·3 c.c. N_2 at 16° and 758 mm. N = 3·9.

$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent.

Attempts to obtain this base in a definite crystalline condition were unsuccessful; it is a colourless, chalky powder which melts to

a gum at about 80—85°. The solution in acetic acid is colourless and gives, on the addition of sulphuric acid, a deep yellow liquid which gradually becomes orange, port-wine coloured, and then cherry-red. The base dissolves readily in hot dilute hydrochloric acid and, on cooling, glistening prisms separate which melt at 223—225° and have all the properties of the hydrochloride (*A*) from which the base was prepared.

*Action of Benzoyl Chloride on Hydroxy*iso*anhydrodihydrocryptopine* (*A*).

In this experiment, the base (1 gram), dissolved in pyridine (4 c.c.) was mixed with benzoyl chloride (1 gram) and heated on the steam-bath when, in a few minutes, the whole set to a creamy mass. After heating for half an hour, the product was stirred with water, the aqueous liquid decanted from the pasty mass, and this again treated with water; the mass was then shaken with ether, the cream collected, and thoroughly washed with ether, in which it is very sparingly soluble. It is also very sparingly soluble in methyl alcohol, and was therefore further purified by boiling with methyl alcohol and collecting. The colourless, satiny mass was dried in the steam-oven and analysed:

0·1054 gave 0·2540 CO_2 and 0·0526 H_2O. C = 65·7; H = 5·5.
0·3406 „ 8·6 c.c. N_2 at 17° and 761 mm. N = 2·9.
0·3091 „ 0·0812 AgCl. Cl = 6·5.

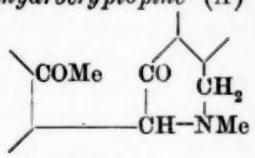
$C_{28}H_{27}O_6N$,HCl requires C = 65·8; H = 5·4; N = 2·7; Cl = 6·9 per cent.

This analysis shows that this substance is the *hydrochloride* of *benzoyloxy*iso*anhydrodihydrocryptopine*,

$$C_{21}H_{22}O_4(O{\cdot}CO{\cdot}C_6H_5)N,HCl.$$

It is beautifully crystalline, and melts at about 235° with evolution of gas to a red syrup, but it is almost insoluble in the usual solvents and could not be recrystallised.

This hydrochloride, suspended in methyl alcohol, is readily decomposed by the addition of a slight excess of cold methyl-alcoholic potassium hydroxide, and a caseous mass separates which is doubtless the benzoyl base. The mass soon hardens and is readily soluble in hot methyl alcohol, from which it separates, on cooling, as a syrup.

Oxidation of Hydroxyisoanhydrodihydrocryptopine (*A*) *to Diketotetrahydroanhydrocryptopine*,  .

The base (3 grams), dissolved in acetone (100 c.c.), was gradually mixed at the ordinary temperature with finely powdered potassium permanganate (3 grams) when oxidation took place very slowly.

The product was filtered, the manganese precipitate washed with acetone, dried, and extracted with hot water, but the aqueous solution was nearly colourless, and gave no precipitate on the addition of hydrochloric acid. The almost colourless acetone extract yielded, on evaporation, a pale yellow syrup, and since this was found to contain some unchanged base (*A*), it was dissolved in dilute hydrochloric acid (1:3) and left for a fortnight in the ice-chest. After decanting from the small quantity of hydrochloride which had separated, the solution gave, on the addition of ammonia, a chalky precipitate which was extracted with much ether and the ethereal solution repeatedly washed with small quantities of very dilute acetic acid. It was then washed with water, dried over potassium carbonate, evaporated to a small bulk, and left in the ice-chest, when small, nodular masses separated which were collected and washed with a little ether:

0·1051 gave 0·2542 CO_2 and 0·0565 H_2O. C = 65·9; H = 5·9.

$C_{21}H_{21}O_6N$ requires C = 65·7; H = 5·5 per cent.

Diketotetrahydroanhydrocryptopine melts at about 185—190°, but this value is only approximate, since the amount of available material was too small to allow of recrystallisation. It dissolves in hot dilute hydrochloric acid to a yellow solution which clouds on cooling, and the deep yellow solution in glacial acetic acid is apparently completely dissociated, on dilution with water, with separation of the base.

The solution in glacial acetic acid remains pale yellow on the addition of sulphuric acid.

Hydroxyisoanhydrodihydrocryptopine (*A*) *Methosulphate*, $C_{21}H_{23}O_5N,Me_2SO_4$.—This substance was prepared by dissolving the base (1 gram) in a little warm benzene and adding pure methyl sulphate (1 c.c.), when the clear solution soon clouded and deposited a syrup which, on rubbing, quickly solidified. The crystalline mass was collected, washed with benzene, and left exposed to the air until free from the

solvent; it was then recrystallised from water, in which it is rather sparingly soluble, and from which it separates in glistening groups of thin, rectangular plates:

0·1096 gave 0·2231 CO_2 and 0·0580 H_2O. C=55·5; H=5·9.
$C_{21}H_{23}O_5N,Me_2SO_4$ requires C=55·7; H=5·8 per cent.

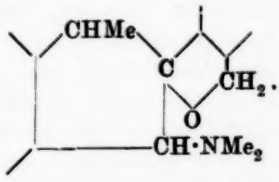
This methosulphate remains bright in the steam-oven, it becomes yellow above 170°, orange at 185°, and melts at 190—192° with effervescence to an orange froth. It is very sparingly soluble even in boiling methyl alcohol and separates, on cooling, in groups of thin plates.

The solution of a crystal in glacial acetic acid gives, on the addition of sulphuric acid, an intense greenish-brown coloration.

The Methiodide, $C_{21}H_{23}O_5N,MeI$.—A hot, fairly concentrated aqueous solution of the methosulphate gives, on the addition of a hot dilute solution of potassium iodide, a clear liquid, from which a beautifully crystalline iodide gradually separates in curiously striated prisms or twin crystals. This begins to darken at 180° and melts at about 200—202° with effervescence to an orange froth; it is very sparingly soluble even in boiling methyl alcohol, and crystallises well in minute colourless prisms:

0·1051 gave 0·1985 CO_2 and 0·0482 H_2O. C=51·1; H=5·1.
$C_{22}H_{26}O_5NI$ requires C=51·6; H=5·1 per cent.

iso*Methylcryptopine* (*β*),



This substance is obtained when the methosulphate of hydroxy*iso*-anhydrodihydrocryptopine (*A*) is decomposed by alkali hydroxides. The hot concentrated aqueous solution of the methosulphate gives, on the addition of sodium hydroxide (30 per cent.), a milky liquid, and a caseous mass soon separates which gradually hardens. This was collected, finely ground, washed thoroughly, and dried over phosphoric oxide in a vacuum desiccator:

0·1186 gave 0·3009 CO_2 and 0·0697 H_2O. C=69·1; H=6·5.
$C_{22}H_{25}O_5N$ requires C=68·9; H=6·5 per cent.

iso*Methylcryptopine* (*β*) is a transparent, yellow resin, and all attempts to obtain it in a crystalline condition have, so far, been unavailing. It is very readily soluble in methyl alcohol and most of the ordinary solvents, and the solution of a trace in a drop of acetic acid gives, on the addition of sulphuric acid, an intense

indigo-blue coloration. The base dissolves very readily in dilute hydrochloric acid, yielding a pale yellow solution which gives, with potassium iodide, a sparingly soluble, chalky precipitate of *iso-methylcryptopine* (*β*) *hydriodide*. This was collected, dissolved in boiling alcohol, and the filtered solution left in the ice-chest, when an ochreous, rather indefinitely crystalline mass gradually separated:

0·1116 gave 0·2131 CO_2 and 0·0517 H_2O. C = 52·1; H = 5·1.
$C_{22}H_{25}O_5N,HI$ requires C = 51·6; H = 5·1 per cent.

The *platinichloride* was obtained, on the addition of platinic chloride to the dilute solution of the hydrochloride, as a chalky mass which was thoroughly washed and dried at 80°:

0·1119 gave 0·1898 CO_2 and 0·0463 H_2O. C = 46·2; H = 4·6.
$(C_{22}H_{25}O_5N)_2,H_2PtCl_6$ requires C = 46·2; H = 4·5 per cent.

This salt darkened at 205°, was black at 220°, and decomposed completely at about 250—255°, with evolution of gas, to a black froth.

iso*Methylcryptopine* (*β*) *Methosulphate*.—*iso*Methylcryptopine (*β*) (1 gram) is readily soluble in benzene, and yields, on the addition of methyl sulphate (2 grams), an immediate precipitation of the methosulphate as a viscid, pale brown syrup which gradually hardens. The benzene was decanted, the syrup washed with benzene, dissolved in methyl alcohol, and mixed with a large excess of methyl-alcoholic potassium hydroxide (5 c.c. of 30 per cent.) when, on heating on the steam-bath, the liquid soon became brown and then deep bluish-black and, on diluting with water, a precipitate separated which was almost like indigo and the filtrate was deep purplish-brown. The precipitate did not filter well, and therefore it was thoroughly washed by decantation, drained on porous porcelain, and dried at 100°, when it had the appearance of a dead black powder:

0·1012 gave 0·2575 HO_2 and 0·0528 H_2O. C = 69·4; H = 5·8.
0·2110 „ 5·9 c.c. N_2 at 16° and 759 mm. N = 3·3.
$C_{23}H_{23}O_5N$ requires C = 70·2; H = 5·8; N = 3·6 per cent.

This remarkable substance is sparingly soluble in the usual solvents, but dissolves in much boiling alcohol to a deep sage-green solution which, on long boiling, becomes brown. It is soluble in hydrochloric acid to an intense sage-green solution, and this becomes brown and clouds on the addition of water. Acetic acid dissolves the black base readily to a deep brown solution which is not precipitated by water, and the addition of much sulphuric acid to a speck of the substance dissolved in a drop of acetic acid gives an intense indigo colour which is not destroyed by diluting with a little water.

It seems that this base is derived from methyl*iso*methylcryptopine (*B*) by the removal of four atoms of hydrogen, due, partly, at least, to oxidation in the air—$C_{22}H_{27}O_5N - 4H = C_{23}H_{23}O_5N$—and a black base, probably identical with this, is also produced from methyl *ψ*-anhydrocryptopine by conversion into the methosulphate and treatment with methyl-alcoholic potassium hydroxide (compare p. 1006).

*Hydroxy*iso*anhydrodihydrocryptopine* (*B*).

The hydrochloride of this base is contained in the mother liquors from the crystallisation of the hydrochloride of the (*A*) modification (p. 995). After remaining for several days, the solution is filtered from a small quantity of impure (*A*) salt and evaporated considerably when, on keeping in the ice-chest, a crust of prisms gradually forms, and more is obtained from the mother liquor by leaving over sulphuric acid in a vacuum desiccator; finally, a viscid, brown syrup remains in small quantity, from which nothing crystalline could be obtained.

The various crops were collected and repeatedly recrystallised from water:

0·1091 gave 0·2494 CO_2 and 0·0607 H_2O. C = 62·3; H = 6·2.

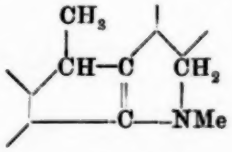
$C_{21}H_{23}O_5N$,HCl requires C = 62·1; H = 5·9 per cent.

*Hydroxy*iso*anhydrodihydrocryptopine hydrochloride* (*B*) melts with frothing at 175—177°, whereas the (*A*) modification melts under the same conditions at 227°. It is rather sparingly soluble in water and separates, when the solution in hot water is allowed to cool slowly, in glistening prisms which are quite different in appearance from the needles of the (*A*) modification and the melting point is not altered by repeated recrystallisation from water. When, however, the salt is boiled for several minutes with methyl alcohol, in which it is readily soluble, and the solution concentrated and allowed to remain, a crystalline salt separates which melts at 225—227° and is the hydrochloride of the (*A*) modification. The mother liquor gives, after boiling with water until the methyl alcohol has been removed and subsequent concentration, a large crop of the unchanged hydrochloride (*B*) melting at 174—177°, so that partial conversion of the (*B*) into the (*A*) modification takes place in these circumstances. The reverse change was brought about in an experiment in which the pure hydrochloride (*A*) was heated with a large excess of acetyl chloride in a sealed tube in the steam-bath for half an hour. After distilling off the acetyl chloride, the residue was boiled with water and the solution concentrated when, on keeping, prisms separated which melted at 175—177° with effervescence and consisted of the hydrochloride (*B*). An experiment

was also made to see if transformation of the hydrochloride (*B*) into the modification (*A*) could be brought about by seeding with a crystal of (*A*), but, when a hot solution of a considerable quantity of the (*B*) modification, just as it was on the point of crystallising, was mixed with a few crystals of (*A*) and vigorously stirred, the crystallisation was still the pure (*B*) hydrochloride.

The addition of dilute ammonia to the aqueous solution of the hydrochloride (*B*) produces an amorphous precipitate which, on analysis, yields numbers agreeing with the formula $C_{21}H_{23}O_5N$ (Found, C=68·0; H=6·3. $C_{21}H_{23}O_5N$ requires C=68·3; H=6·2 per cent.), and evidently consists of hydroxy*iso*anhydrodihydrocryptopine (*B*), since, on solution in dilute hydrochloric acid, it regenerates the hydrochloride (*B*).

iso*Anhydrocryptopine*,



This substance has been obtained in several different ways.

(I) *From Anhydrocryptopine by the Action of Dilute Hydrochloric Acid.*—When the solution of anhydrocryptopine (1 gram) in concentrated hydrochloric acid (2 c.c.) and water (8 c.c.) is heated on the steam-bath for two hours, the deep orange-brown liquid becomes milky on cooling, and deposits a slimy, brown syrup. On the addition of sodium hydroxide to the warm, dilute solution of this syrup, a gelatinous base separates, and when the whole is shaken with ether, part of this dissolves, leaving a semi-solid, brown resin. This resin is readily soluble in boiling methyl alcohol and, on keeping for several days in the ice-chest, a pale brown crust of crude *iso*anhydrocryptopine separates. The ethereal extract yields also a considerable crop of the same substance when it is dried over potassium carbonate, concentrated, and left in the ice-chest. The crops were combined and crystallised from methyl alcohol, from which the new base separated in colourless prisms (m. p. 158°).

(II) *From Hydroxyisoanhydrodihydrocryptopine* (*A*) *or* (*B*) *by the Action of Hydrochloric Acid.*—When either of these bases is dissolved in concentrated hydrochloric acid and the solution boiled for two minutes, the product, on cooling and rubbing, deposits a crystalline hydrochloride. After recrystallisation from hot water, this melts at 237° and consists of the hydrochloride of *iso*anhydrocryptopine, since the base, which is deposited when its aqueous solution is mixed with sodium hydroxide, separates from methyl alcohol in prisms and melts at 157—159°.

(III) *From Hydroxyisoanhydrodihydrocryptopine Hydrochloride* (*A*) *by Means of Phosphoryl Chloride.*—The finely divided hydrochloride (1 gram) dissolves readily in phosphoryl chloride (4 c.c.) and, on heating on the steam-bath, effervescence, due to the evolution of hydrogen chloride, takes place.

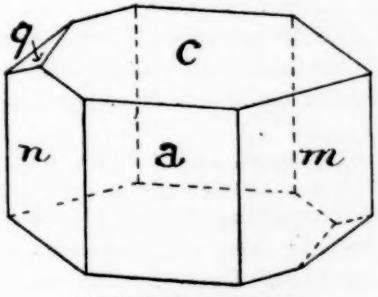
After fifteen minutes, the excess of phosphoryl chloride was removed by distillation from the steam-bath under diminished pressure, and the pale green syrup mixed with ice, when a clear solution resulted which, on rubbing, deposited the sparingly soluble hydrochloride of *iso*anhydrocryptopine. This was collected, recrystallised, and decomposed by sodium hydroxide, when a caseous mass separated which crystallised from methyl alcohol in prisms, melted at 157—159°, and consisted of *iso*anhydrocryptopine. This method seems to be the most satisfactory for the preparation of this substance, since the yield is at least 80 per cent. of that theoretically possible, and the product is much more readily purified than in the cases of methods (I) and (II). The two specimens analysed were made according to methods (I) and (III):

0·1035 gave 0·2713 CO_2 and 0·0563 H_2O. C = 71·5; H = 6·0.
0·1138 „ 0·2991 CO_2 „ 0·0621 H_2O. C = 71·8; H = 6·1.
0·2384 „ 8·4 c.c. N_2 at 15° and 756 mm. N = 4·1.

$C_{21}H_{21}O_4N$ requires C = 71·8; H = 6·0; N = 4·0 per cent.

iso*Anhydrocryptopine* melts at 158—160° without decomposition and is characterised by the facility with which it crystallises. It is sparingly soluble in cold methyl alcohol, but dissolves readily on

FIG. 7.



iso*Anhydrocryptopine.*

boiling, and separates beautifully in glistening, well-developed, short, colourless prisms. It is readily soluble in benzene, chloroform, or ethyl acetate, but sparingly so in light petroleum or ether, and crystallises well from a mixture of benzene and light petroleum in brilliant tablets with bevelled edges.

Mr. T. V. Barker finds the crystals to be triclinic with axial ratios: $a:b:c=0{\cdot}6514:1:0{\cdot}794$; $\alpha=90°58'$, $\beta=120°20'$, $\gamma=102°43'$ (Fig. 7.)

Of the following forms, $c\{001\}$, $a\{100\}$, $m\{110\}$, $n\{1\bar{1}0\}$, and $q\{0\bar{1}1\}$, the latter was only observed on one crystal, so that the value of the axial ratio $c:b$ is not very trustworthy. The following table summarises the results obtained from the measurement of three crystals:

Table of Measured and Calculated Angles.

	ϕ			ρ		
Face.	Limits.	Mean.	Calc.	Limits.	Mean.	Calc.
a (100)	—	90°0′	90°0′	—	90° 0′	90°0′
m (110)	64°13′— 65°43′	*64 48	—	—	90 0	90 0
n (1$\bar{1}$0)	121 49 —123 14	*122 27	—	—	90 0	90 0
c (001)	88 3 — 88 55	*88 25	—	31°28′—31°57′	*31 38	—
q (0$\bar{1}$1)	—	152 16	152 57	—	*41 6	—

Optics: extinction on *c*(001) makes an angle of 36°, with the edge *ca*, and 11° with the edge *cm*. Through the face *c* an optic axis is observed in convergent light.

The solution of a crystal in a drop of acetic acid gives, with sulphuric acid, a deep yellow solution which gradually becomes bright crimson and, on the addition of a little water, brown.

The Hydrochloride.—This fine salt is sparingly soluble in water and still less so in dilute hydrochloric acid and separates, when its solution in boiling very dilute hydrochloric acid is allowed to cool slowly, in glistening, colourless prisms:

0·3157 gave 0·1141 AgCl. Cl=8·9.

$C_{21}H_{21}O_4N,HCl$ requires Cl=9·2 per cent.

When heated rapidly in a capillary tube, this hydrochloride begins to darken at 210°, and melts and decomposes at about 237° to a black froth.

The *hydriodide* is obtained, on the addition of hot dilute potassium iodide to the boiling solution of the hydrochloride, as a viscid precipitate which, on rubbing, suddenly crystallises and is very sparingly soluble both in water and in alcohol:

0·2587 gave 0·1251 AgI. I=26·1.

$C_{21}H_{21}O_4N,HI$ requires I=26·5 per cent.

This salt is very stable and remains almost colourless until 200°; it darkens considerably at 230° and melts at about 240° with vigorous decomposition to a black froth. *iso*Anhydrocryptopine dissolves very readily in dilute sulphuric acid and, on keeping, the *sulphate* separates as a voluminous mass of white hairs or, if the solution is dilute, in masses of slender needles: it is comparatively

readily soluble in water. A paste of the base with water is converted by dilute nitric acid into the *nitrate*, which becomes viscid on boiling, but, when rubbed, crystallises at once. This salt is very sparingly soluble in cold water, and the hot solution, if rapidly cooled, becomes milky even when a crystal is present, but, on stirring, the nitrate separates in glistening, four-sided tablets with cut-off corners or in stout prisms like sugar crystals. When the nitrate is boiled with very dilute nitric acid, the solution becomes immediately yellow and vigorous oxidation rapidly sets in. The *picrate* is a chrome-yellow, amorphous powder, somewhat soluble in boiling water, and the addition of mercuric chloride to the solution of the hydrochloride gives a white, amorphous precipitate which is rather readily soluble in boiling water and separates, on cooling, as an indistinct, crystalline, chalky precipitate. The *platinichloride* separates, on the addition of platinic chloride to the warm solution of the hydrochloride in very dilute hydrochloric acid, as a pale ochreous, caseous precipitate which soon becomes chalky. The dry salt, which is nearly colourless, scarcely darkens at 210° and then gradually shrinks, becomes discoloured, and melts and decomposes at about 230—233° to a carbonaceous froth:

0·1038 gave 0·1727 CO_2 and 0·0386 H_2O. C = 45·4; H = 4·1.

$(C_{21}H_{21}O_4N)_2,H_2PtCl_6$ requires C = 45·3; H = 4·0 per cent.

The Methosulphate.—*iso*Anhydrocryptopine (1 gram), dissolved in a little benzene, was mixed with methyl sulphate (1 c.c.), when the solution clouded and soon deposited a crystalline precipitate which was collected and washed with benzene. In this condition it was nearly pure, but, for analysis, it was recrystallised from boiling water, in which it is readily soluble, and from which it separates in groups of well-defined, short prisms:

0·1070 gave 0·2285 CO_2 and 0·0557 H_2O. C = 58·2; H = 5·8.

$C_{21}H_{21}O_4N,MeSO_4$ requires C = 57·9; H = 5·9 per cent.

iso*Anhydrocryptopine methosulphate* becomes discoloured above 150°, and melts and decomposes at about 245—248° to a brown froth. It is unusually sparingly soluble in boiling methyl alcohol and separates, on cooling, in glistening, short prisms; it is readily soluble in concentrated hydrochloric acid and the solution, when boiled, becomes deep purple. It dissolves sparingly in glacial acetic acid, and the addition of sulphuric acid causes a deep yellow coloration which, on dilution with water, becomes sage-green.

iso*Anhydrocryptopine Methiodide.*—The hot dilute solution of the methosulphate gives, on the addition of hot dilute potassium iodide, no immediate precipitate, but, in a short time, the iodide separates as a heavy, crystalline mass which, under the microscope, is seen to consist of groups of striated prisms:

0·2596 gave 0·1235 AgI. I = 25·5.

$C_{21}H_{21}O_4N$,MeI requires I = 25·7 per cent.

This methiodide melts at about 233—235° to a black mass and is very sparingly soluble in cold methyl alcohol, but dissolves moderately readily on boiling and crystallises beautifully in well-defined, four-sided plates with bevelled edges.

Action of Alkalis on iso*Anhydrocryptopine Methosulphate. Formation of Methyl-ψ-anhydrocryptopine* (compare p. 864).—The hot concentrated aqueous solution of this methosulphate gives, on the addition of sodium hydroxide (10 per cent.), an immediate milkiness and, on boiling for a few minutes, the solution becomes ochreous and a brown syrup separates, but in comparatively small quantity, and if the liquid is decanted, mixed with sodium hydroxide (30 per cent.), and again boiled, a further quantity of the syrup separates. This sets to a resin on cooling, and is collected, washed, dissolved in dilute hydrochloric acid, and precipitated by ammonia in the cold, when a pale ochreous, gelatinous precipitate forms which on warming becomes chalky. After drying over phosphoric oxide the following analytical results were obtained:

0·1042 gave 0·2746 CO_2 and 0·0595 H_2O. C = 71·9; H = 6·3.

$C_{22}H_{23}O_4N$ requires C = 72·3; H = 6·3 per cent.

Methyl-ψ-anhydrocryptopine has, so far, not been obtained in the crystalline condition. It melts at about 100° to an amber resin and is very readily soluble in alcohol, benzene, or ethyl acetate, yielding yellow solutions. The hydrochloride and sulphate are readily soluble, but the *hydriodide* is precipitated, on the addition of potassium iodide to the solution of the hydrochloride, as a caseous precipitate which becomes chalky on warming. This salt is comparatively readily soluble in hot water, quite readily so in methyl alcohol, and was recrystallised from water, from which it separated as a bright yellow, chalky powder which had no definite melting point:

0·1055 gave 0·2085 CO_2 and 0·0475 H_2O. C = 53·8; H = 5·0.

$C_{22}H_{23}O_4N$,HI requires C = 53·5; H = 4·9 per cent.

When *iso*anhydrocryptopine methosulphate is warmed with methyl-alcoholic potassium hydroxide (25 per cent.) it dissolves readily and, on boiling, decomposition sets in gradually with the formation of a red, ochreous, semi-solid mass, which is doubtless crude methyl-ψ-anhydrocryptopine. If, however, the boiling is continued for a few minutes and the methyl alcohol evaporated, the mass becomes deep blue and then bluish-green and, on the addition of water, a fine, indigo-blue base separates which, on shaking with air, becomes green and then greenish-brown. This base dissolves in acetic acid to a brown solution which, on the addition of

sulphuric acid, develops an intense greenish-indigo coloration, and it is probable that this base is closely allied to the base possessing similar properties which was obtained from *iso*methylcryptopine (*β*) methosulphate by the action of methyl-alcoholic potassium hydroxide under the same conditions (compare p. 1001).

The Action of Dilute Sulphuric Acid on Anhydrocryptopine.

In order to secure further confirmation of the interpretation of the results obtained during the study of the action of dilute hydrochloric acid on anhydrocryptopine, which are described in the preceding pages, the behaviour of anhydrocryptopine towards dilute sulphuric acid was investigated. When the base (2 grams) was mixed with sulphuric acid (0·8 c.c.) and water (9 c.c.) and the solution heated on the steam-bath for forty minutes, a syrupy mass separated, the sides of the flask were covered with pale yellow nodules, and, on shaking vigorously, a considerable amount of a crystalline meal separated. The nodules melted roughly at 136° with effervescence, and were rather sparingly soluble in hot water, and the whole, including the syrupy mass, was dissolved in just sufficient boiling water and the solution allowed to cool slowly with constant stirring. The first crop of pale ochreous nodules consisted of the almost pure *hydrogen sulphate* of *hydroxy*iso*anhydrodihydrocryptopine* (*A*) and, after recrystallisation, yielded the following analytical result:

0·1068 gave 0·2099 CO_2 and 0·0529 H_2O. C = 53·6; H = 5·5.

$C_{21}H_{23}O_5N,H_2SO_4$ requires C = 54·0; H = 5·3 per cent.

This salt melts at about 174° with decomposition to a yellow froth, and the proof that it is the salt of base (*A*) (compare p. 996) was obtained in the following way. The salt, dissolved in hot water, was mixed with excess of dilute ammonia and the chalky base collected, washed thoroughly, and dissolved in boiling very dilute hydrochloric acid when, on keeping, glistening prisms separated which melted at 227° and consisted of pure hydroxy*iso*anhydrodihydrocryptopine hydrochloride (*A*), as a careful comparison clearly demonstrated.

*Hydroxy*iso*anhydrodihydrocryptopine Hydrogen Sulphate* (*B*).—The brown mother liquors from the crystallisation of the salt (*A*) were allowed to concentrate over sulphuric acid in a vacuum desiccator until a second small crop of crystals, consisting partly of nodules and partly of prisms, had been deposited. The filtrate from this second crop was further concentrated, and deposited hard crusts of colourless prisms almost like sugar crystals and entirely different from the nodules of the hydrogen sulphate (*A*). These were recrystallised from a small quantity of water and again

obtained in colourless prisms which, under the microscope, looked like striated octahedra, and these, on drying in the steam-oven, became opaque and fell to a chalky powder:

0·1043 gave 0·2065 CO_2 and 0·0520 H_2O. C = 54·0; H = 5·5.

$C_{21}H_{23}O_5N,H_2SO_4$ requires C = 54·0; H = 5·3 per cent.

Hydroxyisoanhydrodihydrocryptopine hydrogen sulphate (*B*) decomposes at about 178—180° to a yellow froth and is more soluble in water than the nodules of the salt (*A*). The addition of ammonia to the aqueous solution yielded a chalky base which, after cllecting and thoroughly washing, was dissolved in hot very dilute hydrochloric acid. On keeping in the ice-chest for several days well-developed, colourless prisms gradually separated which melted at 174—175° and consisted of the hydrochloride of hydroxy*iso*-anhydrodihydrocryptopine (*B*), and this result proves that the hydrogen sulphate just described is, as a fact, the salt of this base (*B*) (compare p. 1001).

Section X.

The epi*Cryptopines, A, B, and C.* (Formulæ, pp. 866, 867.)

The starting point in the investigation of this difficult and interesting section is the conversion of anhydrocryptopine into the hydrochlorides of *epi*cryptopine, *A* and *B*, by the action of concentrated hydrochloric acid (compare p. 865). Anhydrocryptopine (1 gram) is mixed in a test-tube with ordinary concentrated hydrochloric acid (5 c.c.), warmed until dissolved, and then boiled vigorously for forty-five seconds in such a way that the solution becomes considerably concentrated. A pale pink colour soon develops, which rapidly becomes orange-red and ultimately deep crimson, and on the addition of two volumes of water, a chalky precipitate gradually forms and the whole sets to a thin, bright pink paste. When the mass is transferred to the pump, the slimy, chalky precipitate tends to close up the pores of the filter paper, so that filtration is a slow and tedious operation, and, when as complete as possible, the hydrochloride is ground up with dilute hydrochloric acid and again transferred to the filter, and, after a second washing of the same kind, the precipitate is left in contact with porous porcelain for a couple of days. The deep crimson filtrate deposits, on keeping for some weeks, a small crop of a crimson salt, to which the colour of the solution is due, and the examination of this salt is described on p. 1016. The almost colourless hydrochloride is now dissolved in much boiling water, mixed with excess of ammonia, and the caseous precipitate rapidly extracted with much ether. The yellowish-green ethereal solution, which exhibits a striking blue fluorescence, is dried over potassium carbonate, concentrated con-

siderably, and left for some days in the ice-chest, when a hard crust of *epi*cryptopine, *A*, will have separated, but it is usually small in amount. The mother liquor is decanted, the crystalline mass washed thoroughly with ether, and is then almost pure, but it may be recrystallised from methyl alcohol if the operation is rapidly carried out with small quantities (compare p. 1011), but it is better to use benzene as the solvent. Only a small quantity of the *epi*cryptopine, *A*, used in the subsequent experiments was obtained in this way; most of this substance was prepared from *epi*cryptopine, *B*, by the action of dilute hydrochloric acid (p. 1012). The analysis of *epi*cryptopine, *A*, gave the following results:

0·1151 gave 0·2864 CO_2 and 0·0661 H_2O. C = 67·9; H = 6·4.

0·1538 „ 5·4 c.c. N_2 at 17° and 760 mm. N = 4·0.

$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent.

epi*Cryptopine*, *A*, melts at 210—212° and, like cryptopine itself, is characterised by its sparing solubility in the usual organic solvents.

It dissolves with difficulty in boiling methyl alcohol and separates, on cooling, in microscopic, glistening prisms; boiling benzene also dissolves it with difficulty, and the solution, after concentrating, deposits the substance in pale ochreous crusts. It is also sparingly soluble in boiling acetone or methyl ethyl ketone, more readily so in ethyl acetate, and dissolves freely in hot acetophenone without darkening. The solution in acetic acid gives, on the addition of sulphuric acid, an almost colourless solution, which gradually becomes very pale pink; if, however, the solution in acetic acid is boiled for a few seconds, cooled, and then mixed with sulphuric acid, a yellow solution is obtained which rapidly becomes port-wine colour, a colour change which is evidently due to the formation of *epi*cryptopine, *C*, (compare p. 1012). This colour reaction is very useful, because it is so very different from the bluish-violet exhibited by cryptopine under the same conditions, and it therefore serves as a ready means for distinguishing between these substances which, in many of their properties, are so strikingly alike that they may well be easily mistaken for one another.

The Salts of epi*Cryptopine*, *A*. *The Hydrochloride*, $C_{21}H_{23}O_5N,HCl$.—When a paste of the base with water is mixed with excess of dilute hydrochloric acid, a jelly is produced, just as in the case of cryptopine, and this breaks up on gently warming and yields a chalky precipitate, which was collected and well washed. This hydrochloride is very sparingly soluble in boiling water, but, when once dissolved, it does not readily separate again, but does so immediately on the addition of dilute hydrochloric acid. It was collected,

washed with dilute hydrochloric acid, drained on porous porcelain, and dried in the steam-oven in the dark, since it has a tendency to discolour when it is exposed to sunlight:

0·1214 gave 0·2736 CO_2 and 0·0677 H_2O. C = 61·5; H = 6·2.
0·2968 „ 0·1031 AgCl. Cl = 8·6.
$C_{21}H_{23}O_5N$,HCl requires C = 62·1; H = 5·9; Cl = 8·7 per cent.

The Hydriodide, $C_{21}H_{23}O_5N$,HI.—A boiling solution of the hydrochloride yields, on the addition of a hot solution of potassium iodide, a milky liquid which almost immediately crystallises, and the chalky precipitate is seen under the microscope to consist of warty masses. It is somewhat soluble in water, and separates on cooling as a chalky, crystalline powder. The dry salt is a brittle mass like porcelain, which begins to darken at 210° and melts at 230—232° with much effervescence to a dark red froth:

0·1016 gave 0·1884 CO_2 and 0·0468 H_2O. C = 50·7; H = 5·1.
0·1434 „ 0·0685 AgI. I = 25·8.
$C_{21}H_{23}O_5N$,HI requires C = 50·7; H = 4·8; I = 25·6 per cent.

The *platinichloride* is obtained as a very pale ochreous precipitate when platinic chloride is added to the hot aqueous solution of the hydrochloride:

0·1161 gave 0·1878 CO_2 and 0·0423 H_2O. C = 44·1; H = 4·1.
0·2442 „ 0·0424 Pt. Pt = 17·4.
$(C_{21}H_{23}O_5N)_2,H_2PtCl_6$ requires C = 44·0; H = 4·2; Pt = 17·0 per cent.

The solution of the hydrochloride gives, with mercuric chloride, a milky liquid which, on warming, deposits a very sparingly soluble, crystalline precipitate and, with picric acid, a very sparingly soluble, chrome-yellow precipitate which softens to a resin on boiling with water.

The Acetyl Derivative, $C_{21}H_{22}O_4N(O{\cdot}CO{\cdot}CH_3)$.—The ease with which *epi*cryptopine, *A*, yields the acetyl derivative is remarkable. When the finely powdered substance is mixed with acetic anhydride in the cold it dissolves, and almost immediately crystallisation commences and the acetyl derivative separates as a glistening, crystalline powder. This was collected and washed, first with acetic anhydride and then with methyl alcohol, and dried in the steam-oven:

0·1024 gave 0·2513 CO_2 and 0·0556 H_2O. C = 66·9; H = 6·0.
0·3500 „ 9·8 c.c. N_2 at 18° and 763 mm. N = 3·5.
$C_{23}H_{25}O_6N$ requires C = 67·1; H = 6·1; N = 3·4 per cent.

This acetyl derivative darkens at about 285° and melts at about 290° to a deep brown liquid. It is very sparingly soluble in boiling alcohol, benzene, chloroform, methyl ethyl ketone, acetic anhydride, or cold acetic acid, but it dissolves in much boiling acetic acid, appa-

rently with some change, since it does not separate again even on long keeping. It is remarkably resistant to hydrolytic agents. Thus the crystals are coloured green by concentrated hydrochloric acid and dissolve on boiling to a yellowish-brown solution, and the addition of ammonia gives a caseous precipitate, which crystallises from much ether in crusts, melts at 290°, and consists of the unchanged acetyl derivative. Again, it does not appear to be appreciably hydrolysed when boiled with concentrated methyl-alcoholic potassium hydroxide, and it does not seem to be readily affected by boiling with aniline.

Conversion of epi*Cryptopine, A, into* epi*Cryptopine, B.*—It has already been mentioned that *epi*cryptopine, *A*, is very sparingly soluble in methyl alcohol, but on heating in a sealed tube with methyl alcohol at 100°, it gradually dissolves and, on cooling, nothing separates even after considerable concentration. The addition of water produces a voluminous, chalky precipitate which was extracted with ether, the ethereal solution was then thoroughly washed with water, dried over potassium carbonate, and evaporated, when an almost colourless resin remained which had all the properties of *epi*cryptopine, *B*, (see below).

epi*Cryptopine* (*B*).

When the ethereal mother liquor from the crystallisation of *epi*cryptopine, *A*, (compare p. 1009) is concentrated and left in the ice-chest for a week it yields only a thin crust of the same substance, and the ethereal solution, on complete evaporation, leaves a large quantity of a pale brown resin which is by far the main product of the action of hydrochloric acid on anhydrocryptopine and subsequent decomposition of the mixed *epi*cryptopine hydrochlorides by ammonia. The resin was dissolved in cold dilute hydrochloric acid, and the sparingly soluble hydrochloride which separated washed thoroughly and recrystallised from water; it was then dissolved in hot water, decomposed by ammonia, and the base extracted with ether. After drying over potassium carbonate, the ether was evaporated and the residue left first over sulphuric acid and then over phosphoric oxide in a vacuum desiccator, when it frothed up and ultimately became quite brittle, like flakes of almost colourless shellac:

0·1385 gave 0·3445 CO_2 and 0·0804 H_2O. C = 67·8; H = 6·4.

0·4012 „ 13·1 c.c. N_2 at 17° and 758 mm. N = 3·9.

$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent.

epi*Cryptopine, B*, differs from the modifications, *A*, and *C*, in that it is very readily soluble in ether, alcohol, and most other solvents, and exhibits no tendency to assume the crystalline condition.

The *platinichloride* was obtained as a very pale salmon precipitate when platinic chloride was added to the warm solution of the hydrochloride:

0·1126 gave 0·1818 CO_2 and 0·0441 H_2O. C = 44·0; H = 4·3.

0·2225 „ 0·0372 Pt. Pt = 16·7.

$(C_{21}H_{23}O_5N)_2,H_2PtCl_6$ requires C = 44·0; H = 4·2; Pt = 17·0 per cent.

The Acetyl Derivative.—*epi*Cryptopine, *B*, dissolves readily in acetic anhydride, yielding a brown solution, and when this is boiled and, if necessary, concentrated, a heavy, crystalline precipitate separates. This was collected, washed with acetic anhydride, and then with methyl alcohol, and the mother liquor, on mixing with twice the volume of methyl alcohol, deposited a considerable crop of the same substance. This acetyl derivative darkened at 280° and melted at about 290—295° to a brown mass, and had exactly the appearance and properties of the acetyl derivative of *epi*cryptopine *A*. (Found, C = 66·9; H = 6·0; N = 3·4. $C_{23}H_{25}O_6N$ requires C = 67·1; H = 6·1; N = 3·4 per cent.)

Conversion of epi*Cryptopine, B, into* epi*Cryptopine, A*.—It has already been shown (p. 1011) that *epi*cryptopine, *A*, is converted into the modification, *B*, when it is boiled with methyl alcohol, and the reverse change may be brought about by the action of hydrochloric acid. When *epi*cryptopine, *B*, is mixed with excess of very dilute hydrochloric acid (1 in 10), and heated on the steam-bath, it dissolves to a clear solution, but soon the hydrochloride of *A* begins to separate in very sparingly soluble crusts. It was collected, washed well, ground up with water and excess of ammonia, and shaken with ether, when much remained undissolved. The precipitate was collected, washed with ether and then with water, and dried in the steam-oven, when it melted at 190—195° and, after recrystallising from benzene, at 210—212°, and consisted of pure *epi*cryptopine, *A*, the yield being about 60 per cent. of the original *epi*cryptopine, *B*. The ethereal mother liquor left, on evaporation, the remaining 40 per cent. as a resin, which apparently consisted of unchanged *epi*cryptopine, *B*.

epi*Cryptopine* (*C*).

The curious change of *epi*cryptopine, *A*, to the acetate of *C* was discovered accidentally during the recrystallisation of *A* from ethyl acetate which had been carefully freed from acetic acid by contact with potassium carbonate. About 5 grams of *A* were boiled with much ethyl acetate, in which it is very sparingly soluble, and after about an hour the solution was concentrated, during which a pale lemon, glistening mass separated from the hot liquid, and this melted at 208—210° and consisted of unchanged *A*. After filtering, the filtrate was concentrated considerably and left in the ice-chest

for a fortnight, when a chalky, crystalline crust separated which, after collecting and rapidly washing with cold ethyl acetate, melted at 184—185° and consisted of the *acetate* of epi*cryptopine*, *C*:

0·1049 gave 0·2464 CO_2 and 0·0609 H_2O. C = 64·1; H = 6·4.
0·2321 „ 6·5 c.c. N_2 at 13° and 758 mm. N = 3·3.
$C_{21}H_{23}O_5N,C_2H_4O_2$ requires C = 64·3; H = 6·3; N = 3·3 per cent.

This acetate is readily soluble in hot water, but is to some extent dissociated unless a little acetic acid is added, and ammonia gives, with the clear solution, a jelly which, on warming, becomes crystalline.

The precipitate was collected, washed well, and left in contact with porous porcelain; it was then extracted with ether, which readily dissolved the crude base, and left a small, black impurity. The ethereal solution was filtered, washed, dried over potassium carbonate, and concentrated when, on leaving in the ice-chest, a crust of warty groups separated and melted at 165—167° to an almost colourless syrup. The mother liquor yielded on concentration a considerable second crop of rather lower melting point. Subsequently it was discovered that heating with dilute acid readily brings about the transformation of *epi*cryptopine, *A*, into the modification, *C*. If finely divided *epi*cryptopine, *A*, is mixed, in the cold, with dilute acetic acid (15 per cent.) it changes in appearance, becomes colloidal, and impossible to filter. On warming, solution takes place, and if, after heating on the steam-bath for ten minutes, ammonia is added in excess, a caseous precipitate separates which, on cooling, becomes brittle and, when dried over phosphoric oxide, melts at about 115° to a syrup. It is curious that the substance in this condition gives numbers agreeing approximately with those required for *epi*cryptopine. (Found, C = 67·7; H = 6·2. $C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2 per cent.) The brittle mass was dissolved in moist ether, the ethereal solution carefully dried over potassium carbonate, and concentrated, when a thin crust separated on which nodular masses gradually formed, and these two substances could be separated mechanically. The crust melted at 205—207° and consisted of unchanged *epi*cryptopine *A*, whereas the nodules melted at about 162° and, after twice recrystallising from ether, at 165—167° not quite sharply, and consisted of *epi*cryptopine, *C*. In the following analyses (I) was made with material prepared from the acetate, and (II) with a specimen obtained by the acetic acid process just described:

(I) 0·1216 gave 0·3023 CO_2 and 0·0679 H_2O. C = 67·8; H = 6·2.
(I) 0·1705 „ 5·4 c.c. N_2 at 17° and 758 mm. N = 3·7.
(II) 0·1092 „ 0·2711 CO_2 and 0·0611 H_2O. C = 67·9; H = 6·2.
$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent.

epi*Cryptopine*, *C*, is sparingly soluble in ether, but its solution may be concentrated to a very small bulk without crystallisation commencing; it dissolves readily in alcohol, benzene, or acetone. The solution in acetic acid gives, on the addition of sulphuric acid, at first no coloration, then a deep violet gradually develops; a very different reaction from that exhibited by *epi*cryptopine, *A*. It dissolves readily in dilute hydrochloric acid, but, on stirring, a sparingly soluble hydrochloride soon separates as a chalky mass. When *epi*cryptopine, *C*, is warmed with phosphoryl chloride it dissolves to a brown solution, but without the formation of a scarlet salt corresponding with *epi*cryptopirubin chloride (see below). It dissolves also in acetic anhydride and, on warming, the *acetyl* derivative soon begins to separate in spangles which melt at 285—290°, with decomposition, to a black mass. (Found, C = 66·8; H = 6·1. $C_{23}H_{25}O_6N$ requires C = 67·1; H = 6·1 per cent.) This acetyl derivative has properties which, so far as can be judged in the case of so insoluble a substance, are the same as those of the acetyl derivatives obtained from *epi*cryptopine, *A*, and *B*, and there is little doubt that the same substance is produced in all three cases.

The epi*Cryptopirubin Salts.* (Formulæ, p. 873).

The action of phosphoryl chloride on *epi*cryptopine, *A*, is highly characteristic. When this substance (0·5 gram) is heated with phosphoryl chloride (5 c.c.), at first gently and then to boiling, it becomes salmon-coloured and dissolves to an orange solution which soon becomes intense orange-red. The boiling is continued for twenty minutes, most of the excess of phosphoryl chloride distilled off under diminished pressure, during which a red, crystalline substance separates sometimes in considerable quantity. In order to avoid decomposition due to local rise of temperature, it is a good plan to pour the residual, dark red mass in a thin stream round the sides of a small porcelain basin; ice is then added, and the whole left for some hours. On heating to boiling, all dissolves with the exception of a small quantity of an ochreous substance, which was not further examined, and, on cooling the deep crimson solution, it deposits a brilliant scarlet, crystalline precipitate of *epi*cryptopirubin chloride, and this, after recrystallisation from water, was analysed with the following results:

0·1089 gave 0·2587 CO_2 and 0·0554 H_2O. C = 64·8; H = 5·7.

0·2941 „ 0·1048 AgCl. Cl = 8·9.

$C_{21}H_{22}O_4NCl$ requires C = 65·0; H = 5·7; Cl = 9·2 per cent.

epi*Cryptopirubin chloride*, when heated in a capillary tube, does not appear to change below 210°, it becomes brownish-red at 215°

and melts at 220—223° to a blackish-brown froth. The pure salt, which closely resembles red mercuric iodide in appearance, is sparingly soluble in cold water, but dissolves readily on boiling to a solution of the colour of red ink. It also dissolves readily in hot methyl alcohol, and the deep orange-red solution deposits the salt in well-defined, orange-red prisms. The chloride dissolves in acetic acid to a bright orange salt, and the addition of sulphuric acid produces a yellow solution which exhibits a deep yellowish-green fluorescence. The colour rapidly becomes greener and soon an intense sage-green, and this persists even on the addition of a good deal of water. The aqueous solution of the chloride gives a deep greenish-brown solution on the addition of ammonia or sodium carbonate, and when this is warmed a brownish-black, amorphous precipitate separates. When a trace of the chloride, dissolved in water, is covered with a considerable layer of ether and, after the addition of ammonia, the whole rapidly shaken, the ether is coloured deep green and exhibits a blue fluorescence, but the colour soon fades to yellow and a black precipitate separates (compare p. 1016).

A trace of the chloride, mixed with concentrated nitric acid, gives an intense port-wine solution, especially on warming gently.

*epi*Cryptopirubin nitrate is precipitated, on the addition of dilute nitric acid to the hot solution of the chloride, as a crystalline, vermilion precipitate, which is sparingly soluble in hot dilute nitric acid and separates, on cooling, in irregular groups of flat, striated prisms.

The Iodide.—In preparing this salt, potassium iodide was added to the hot solution of the chloride, when the clear liquid immediately began to deposit a splendid deep vermilion precipitate, which was collected and washed with boiling water, in which it is very sparingly soluble:

0·1006 gave 0·1924 CO_2 and 0·0408 H_2O. C = 52·2; H = 4·5.
0·1414 „ 0·0692 AgI. I = 26·4.
$C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·6; I = 26·5 per cent.

This iodide dissolves sparingly in boiling methyl alcohol to an orange-red solution, from which irregular prisms separate on cooling.

The *platinichloride* was obtained by adding platinic chloride to the hot solution of the hydrochloride when a brown, apparently crystalline precipitate separated which was collected, well washed, and dried in the steam-oven. The deep maroon powder decomposes with effervescence at about 205—210° to a reddish-brown mass:

0·1052 gave 0·1729 CO_2 and 0·0367 H_2O. C = 44·8; H = 3·9.
0·2442 „ 0·0424 Pt. Pt = 17·4.
$(C_{21}H_{22}O_4N)_2PtCl_6$ requires C = 45·3; H = 4·0; Pt = 17·5 per cent.

The dilute solution of the chloride gives no precipitate with mercuric chloride, but, in concentrated solutions, a bright yellowish-red precipitate is produced, which dissolves in much boiling water to a yellow solution and separates, on cooling, in short, orange-red prisms. The addition of picric acid to the solution of the chloride produces an orange, amorphous precipitate, which becomes crystalline on boiling and is very sparingly soluble.

Examination of the Mother Liquors from the Preparation of epi*Cryptopine Hydrochloride.*—This deep reddish-brown aqueous solution (p. 1008) was concentrated on the water-bath and allowed to remain, when a scarlet chloride separated in considerable quantity in definite crystals which were collected and dried in the steam-oven. It was then a deep, dull red powder which softened at 145° and melted at 150—155° with effervescence to a red froth, and it is thererore not identical with *epi*cryptopirubin chloride. In all probability this salt, which on analysis gave Cl = 9·4, is dehydro-*epi*cryptopirubin chloride, $C_{21}H_{20}O_4NCl$ (p. 1017; Cl = 9·3 per cent.), and owes its formation to the oxidising action of the air during the long evaporation on the water-bath.

The mother liquor from this salt was covered with much ether in a separating funnel, mixed with excess of sodium hydroxide, and the whole well shaken. The green, ethereal solution exhibited a striking blue fluorescence, soon became yellow, and a dark brownish-black base separated; after filtering from this, drying over potassium carbonate, and concentrating, a brown, ochreous, crystalline powder separated:

0·1102 gave 0·2671 CO_2 and 0·0502 H_2O. C = 66·0; H = 5·4.

$C_{21}H_{19}O_6N$ requires C = 66·1; H = 5·0 per cent.

This base dissolves in dilute hydrochloric acid to a brown solution, and is probably identical with the base of the same composition described in the next section.

*Dehydro*epi*cryptopirubin Hydroxide.*

In order to discover the nature of the base produced by the action of dilute alkalis on *epi*cryptopirubin chloride, a quantity of the very pure scarlet salt was dissolved in hot water, rapidly cooled, and stirred, when the salt separated in a very finely divided condition. It was transferred to a separating funnel, covered with much ether, mixed with potassium hydroxide, and shaken, when the deep green, ethereal solution soon became yellow and a nearly black precipitate separated. The ethereal solution was decanted, the black precipitate collected, and well washed, first with ether and then with water, and dried on porous porcelain in the water-oven. Two different specimens were analysed:

0·1200 gave 0·3020 CO_2 and 0·0596 H_2O. C=68·6; H=5·5.
0·1146 „ 0·2866 CO_2 „ 0·0572 H_2O. C=68·2; H=5·5.
$C_{21}H_{21}O_5N$ requires C=68·6; H=5·7 per cent.

*Dehydro*epi*cryptopirubin hydroxide* is a reddish-black, crystalline powder which, when moistened and rubbed on a piece of porous porcelain, gives a deep reddish-brown streak. It dissolves in much boiling water to a brown solution, which dyes the fingers; it is also somewhat soluble in methyl alcohol to a yellowish-brown solution and dissolves also in acetone or chloroform. When the base is moistened with dilute hydrochloric acid it at once yields a bright red salt which is soluble in boiling water and separates, on cooling, in intense purplish-red crystals. The dry salt is a purplish-red powder almost like amorphous phosphorus in appearance; it changes colour at 140° and softens to a resin at about 155° without showing any definite melting point.

The dilute aqueous solution of the salt is the colour of dichromate and is changed to brown on the addition of dilute ammonia without precipitation; on warming, however, the base separates as a deep brown precipitate.

Potassium iodide, added to the solution of the chloride, gives an intense brick-red iodide which may be recrystallised from water.

The ethereal solution, which had been separated from the black base as described above, was dried over potassium carbonate and concentrated, when, on long keeping, a yellowish-brown, crystalline crust separated:

0·1002 gave 0·2419 CO_2 and 0·0473 H_2O. C=65·9; H=5·2.
$C_{21}H_{19}O_6N$ requires C=66·1; H=5·0 per cent.

There can be little doubt that this base is identical with the substance of the same composition described in the last section, but there is no evidence as to its constitution.

*Keto*isoepi*cryptopirubin Hydrochloride* (p. 874).

This brilliant scarlet salt is produced when ketoanhydrocryptopine reacts with phosphoryl chloride (compare p. 1008). Ketoanhydrocryptopine (1 gram) dissolves in phosphoryl chloride (2·5 c.c.) with some evolution of heat, and when the test-tube containing the orange-brown solution is placed in boiling water there is a good deal of effervescence and the colour changes to deep brown and then to dark red. After fifteen minutes the product is cooled in a freezing mixture, mixed with a little powdered ice, and, as soon as decomposition is complete, the crimson precipitate is collected and washed with concentrated hydrochloric acid. A specimen of the salt which had been left over powdered potassium hydroxide in a

vacuum desiccator until the weight was constant gave the following analytical results:

0·1015 gave 0·2351 CO_2 and 0·0455 H_2O. C = 63·2; H = 4·9.
0·2255 „ 0·0709 AgCl. Cl = 7·8.
$C_{21}H_{19}O_5N$,HCl requires C = 62·8; H = 4·9; Cl = 8·8 per cent.

This salt separates from hot dilute hydrochloric acid as a microcrystalline, deep scarlet precipitate, but not without some hydrolysis taking place, since the salt after recrystallisation contained only 6·5 per cent. of chlorine. The dilute solution in hydrochloric acid, which has exactly the appearance of red ink, gives, on the addition of nitric acid, a deep bluish-crimson precipitate of the sparingly soluble nitrate, and when this is warmed decomposition ensues and an intense violet solution results. The *platinichloride* was obtained, on the addition of platinic chloride to the solution of the rubin chloride, in hydrochloric acid, as an intense crimson precipitate which, when dry, resembled amorphous phosphorus in appearance:

0·1312 gave 0·2145 CO_2 and 0·0423 H_2O. C = 44·6; H = 3·5.
0·2122 „ 0·0368 Pt. Pt = 17·3.
$(C_{21}H_{19}O_5N)_2,H_2PtCl_6$ requires C = 44·2; H = 3·5; Pt = 17·2 per cent.

The aurichloride separates, on the addition of gold chloride to the solution of the hydrochloride in hydrochloric acid, as a deep maroon precipitate.

*Keto*isoepi*cryptopirubin Base*.—When finely powdered keto*isoepi*-cryptopirubin hydrochloride (from which adherent hydrochloric acid had been completely removed by exposure over potassium hydroxide in a vacuum desiccator) was boiled with water, the scarlet solution soon deposited a granular precipitate and much water, and prolonged boiling nearly decolorised the solution. The precipitated base was collected, washed with dilute hydrochloric acid and then with water, drained on porous porcelain, and recrystallised from dilute acetic acid:

0·1001 gave 0·2525 CO_2 and 0·049 H_2O. C = 68·7; H = 5·3.
0·2862 „ 9·6 c.c. N_2 at 10° and 746 mm. N = 4·0.
$C_{21}H_{19}O_5N$ requires C = 69·1; H = 5·2; N = 3·9 per cent.

*Keto*isoepi*cryptopirubin base* shrinks at 210°, gradually darkens as the temperature rises, and melts, not at all sharply, at about 235—240°. It is almost insoluble in cold alcohol, but dissolves somewhat on boiling, and separates as a thin crust of almost colourless prisms; it crystallises from dilute acetic acid in brilliant, well-developed, stout, glistening prisms. The solution in glacial acetic acid develops, on the addition of sulphuric acid, a deep yellow

colour which gradually becomes brown, and a splinter of a crystal dissolves in concentrated nitric acid to an intense violet-red solution. The base is quite insoluble in dilute hydrochloric acid (1 in 6), but it is coloured red by concentrated hydrochloric acid, and dissolves on warming to an intense red solution which, on the addition of water, is largely decolorised with separation of the base.

The epi*Methylcryptopines, A, and B.*

It has already been stated that the methylcryptopines (β) and (γ) are readily attacked by mineral acids with the formation of intensely violet solutions, from which ammonia precipitates ochreous bases which have the same percentage composition as methylcryptopine. The difference in the behaviour of the methylcryptopines (β) and (γ) is, however, striking. When methylcryptopine (γ) is dissolved in concentrated hydrochloric acid a yellow solution is at once produced which rapidly becomes intense crimson, but methylcryptopine (β), under exactly the same conditions, dissolves to a colourless solution which soon becomes a pale greenish-pink. On remaining overnight, however, both solutions acquire the same deep permanganate colour, but on adding two volumes of water to each and leaving for a couple of days the solution of the (γ)-modification deposits a chalky hydrochloride, whereas the other remains clear. In order to obtain some clue as to the nature of these changes the action of concentrated hydrochloric acid on methylcryptopine (γ) was investigated as completely as was possible with the small amount of material available. When this substance (2 grams) is mixed with ordinary concentrated hydrochloric acid (10 c.c.) it is coloured yellow and, on heating in boiling water, it immediately dissolves and the solution soon acquires an intense reddish-violet (permanganate) colour.

After heating for twenty minutes the product was mixed with two volumes of water and allowed to remain for two days, during which a slimy, colourless hydrochloride separated, but in rather small quantity. This was collected and well washed with dilute hydrochloric acid, in which it is very sparingly soluble, and was then almost colourless (the investigation of the deep permanganate-coloured filtrate is described on p. 1022). The hydrochloride was dissolved in much boiling water and excess of ammonia added, when a chalky precipitate separated, which was collected, washed, and dried on porous porcelain. The substance was then shaken with much ether, in which it partly dissolved, leaving a chalky precipitate, which was collected, washed with ether, and recrystallised from benzene, from which the substance separated as a chalky powder:

0·1043 gave 0·2627 CO_2 and 0·0612 H_2O. C = 68·7; H = 6·5.
0·2351 „ 7·3 c.c. N_2 at 16° and 758 mm. N = 3·7.
$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

*epi*Methylcryptopine, *A*, melts at 222—223° and, like *epi*cryptopine, *A*, exhibits little facility for crystallising. It is readily soluble in chloroform, but sparingly so in methyl alcohol, benzene, acetone, or ethyl acetate, and is almost insoluble in light petroleum. The addition of light petroleum to the solution in boiling benzene yields a clear liquid, from which the substance separates as a chalky powder consisting of indefinitely crystalline, warty masses. It also separates as a chalky powder, but very slowly and imperfectly, when its solutions in boiling ethyl acetate or acetone are concentrated and left in the ice-chest.

The solution in acetic acid gives, on the addition of sulphuric acid, at first an almost colourless solution, but, on keeping, this gradually develops a pale salmon tint. If left overnight the solution will have become green, and the addition of a few drops of water produces an intense claret coloration. *epi*Methylcryptopine, *A*, is characterised by the fact that its salts with mineral acids are remarkably sparingly soluble. The hydrochloride is almost insoluble in cold dilute hydrochloric acid, and dissolves only very sparingly on boiling; the iodide and nitrate are colourless and also very sparingly soluble. The sulphate separates, when the finely divided base is warmed with very dilute sulphuric acid, as a chalky powder, which seems to be almost insoluble even in much boiling dilute sulphuric acid. Unlike *epi*cryptopine, *A* (p. 1010), *epi*methylcryptopine, *A*, does not yield a characteristic acetyl derivative; it is sparingly soluble in acetic anhydride in the cold, but dissolves on boiling, and nothing separates even when the solution is concentrated and allowed to remain. In order to compare the behaviour of *epi*cryptopine, *A*, and *epi*methylcryptopine, *A*, towards phosphoryl chloride and so to determine the influence of the extra methyl group in the latter on the possibility of yielding a scarlet chloride (compare p. 1014), the following experiment was made: Freshly distilled phosphoryl chloride (2 c.c.) was added to each of two test-tubes (*a*) and (*b*) containing respectively 1 gram of *epi*cryptopine, *A*, and of *epi*methylcryptopine, *A*, and the tubes were then gradually heated side by side in a sulphuric acid-bath. At 100° the contents of (*a*) rapidly became deep salmon, a caseous precipitate separated, and, after boiling for five minutes, the colour was brick-red; after ten minutes almost the whole of the precipitate had disappeared and the solution had the colour of red ink.

The temperature was then raised and the excess of phosphoryl chloride distilled off, when a deep red, semi-solid mass remained

which, on the addition of water, yielded a large amount of a crystalline precipitate of the scarlet chloride. The mixture of *epi*methylcryptopine, *A*, and phosphoryl chloride contained in the tube (*b*) exhibited a very different behaviour. At 100° a pale green solution was first formed, but this colour rapidly disappeared and the milky liquid deposited a pale ochreous, caseous mass in considerable quantity. At the end of ten minutes there was no sign of a pink coloration and, after distilling off the excess of phosphoryl chloride, an ochreous mass was left which had the properties of a quaternary salt and was sparingly soluble in water.

It is shown on p. 1012 that *epi*cryptopine, *A*, is converted into a new modification, *C*, when it is boiled with dilute acetic acid, but *epi*methylcryptopine, *A*, does not appear to be changed by this treatment. In order to demonstrate this important difference, *epi*methylcryptopine *A* (1 gram) was dissolved in glacial acetic acid (5 c.c.) and water (20 c.c.) and heated on the steam-bath, when the solution became first yellow, then orange, and finally orange-red. After heating for an hour, ammonia precipitated a gelatinous mass which, on warming, became crystalline, and this was collected, washed well, and crystallised from much boiling methyl alcohol, in which it was sparingly soluble and from which it separated as a chalky, crystalline mass which melted at 218—220° and consisted of unchanged *epi*methylcryptopine *A*.

epi*Methylcryptopine*, *B*.—The ethereal mother liquor from the purification of *epi*methylcryptopine, *A*, (p. 1019) was concentrated somewhat and left in the ice-chest for a month; it was then decanted from the very slight precipitate which had separated and evaporated, when a pale orange syrup remained in quantity. This was exposed over sulphuric acid in a vacuum desiccator until it was quite free from ether and the weight had become constant and the friable, ochreous powder of *epi*methylcryptopine, *B*, analysed:

0·1019 gave 0·2551 CO_2 and 0·0585 H_2O. C = 68·3; H = 6·4.

0·2327 „ 7·2 c.c. N_2 at 15° and 752 mm. N = 3·6.

$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

The conversion of *epi*methylcryptopine, *B*, into the modification, *A*, was brought about, as in the corresponding conversion of *epi*cryptopine, *B*, into *A* (p. 1012), by boiling with dilute hydrochloric acid.

The ochreous resin was dissolved in dilute hydrochloric acid (1 in 10) and heated on the steam-bath, when the viscid precipitate which first formed soon became chalky and very sparingly soluble. This hydrochloride was collected, washed until quite free from the pink mother liquor, dissolved in much water, and mixed with excess of ammonia, when a viscid precipitate separated which, on cooling and

stirring, became brittle. This was dried and ground with ether until the unchanged ,*B*, had dissolved and left a colourless, chalky powder which melted at 218° and, after recrystallisation, at 219—221° and consisted of *epi*methylcryptopine, *A*.

The ethereal mother liquor yielded, on evaporation, a resin which, on again heating with dilute hydrochloric acid, gave a further small quantity of the hydrochloride of *epi*methylcryptopine, *A*. *epi*Methylcryptopine, *B*, dissolves readily in phosphoryl chloride to a deep reddish-brown solution and, on heating at 60°, the colour becomes intense brownish-violet. The whole was gently boiled for fifteen minutes, the excess of phosphoryl chloride distilled off under diminished pressure, when water precipitated a dark brown tar and there was no sign of the formation of a crystalline, scarlet salt.

isoepi*Methylcryptopine*.—The product of the action of hydrochloric acid on methylcryptopine (γ) is a sparingly soluble hydrochloride and a deep permanganate-coloured solution and, after filtering from the precipitate (compare p. 1019), the filtrate was rendered alkaline with ammonia, when an ochreous, gelatinous precipitate separated which, on warming, became granular and could be filtered. After washing and drying on porous porcelain, the mass was shaken with much ether, filtered from the considerable slimy residue, the ethereal extract dried over potassium carbonate, concentrated, and left in the ice-chest for several days, but nothing separated.

On evaporating the ethereal solution to dryness an orange resin remained which could be dried in the steam-oven without melting. This substance, which amounts to at least 70 per cent. of the product of the action of hydrochloric acid on methylcryptopine (γ), was dissolved in ether and precipitated by light petroleum into four fractions, of which the second and third gave the following analytical results:

II. 0·1227 gave 0·3130 CO_2 and 0·0720 H_2O. C = 69·5; H = 6·5.
III. 0·0989 „ 0·2521 CO_2 „ 0·0575 H_2O. C = 69·5; H = 6·4.
III. 0·3872 „ 12·7 c.c. N_2 at 739 mm. and 18°. N = 3·7.
$C_{22}H_{25}O_5N$ requires C = 68·9; H = 6·5; N = 3·6 per cent.

This substance, which has been provisionally named 'isoepi*methylcryptopine*,' dissolves in dilute mineral acids, yielding very readily soluble salts, the solutions of which are intensely permanganate-coloured.

The hydrochloride gives, with potassium iodide, a violet, gelatinous precipitate which is soluble in boiling water and separates as an apparently crystalline precipitate. The *platinichloride* is obtained as a purple, gelatinous precipitate when platinic chloride is added to the cold solution of the hydrochloride, and becomes chalky on warming. The dry salt is plum-coloured:

0·1991 gave 0·0333 Pt. Pt = 16·7.

$(C_{22}H_{25}O_5N)_2,H_2PtCl_6$ requires Pt = 16·6 per cent.

A formula, which it is suggested may represent the constitution of *isoepi*methylcryptopine, is given on p. 871.

Section XI.

Protopine, $C_{20}H_{19}O_5N$.

The alkaloid employed in these experiments was pure, and melted sharply at 207°. A trace of the substance, dissolved in a drop of acetic acid, gave, on the addition of sulphuric acid, a deep bluish-violet coloration which gradually became more intense and rapidly so, and at the same time redder in shade, on the addition of two drops of water.

Several of the usual salts of the base have been prepared and analysed by other investigators, and the only salts which are here described are those derived from *iso*protopine, $C_{20}H_{18}O_4N{\cdot}OH$.

iso*Protopine Chloride*, $C_{20}H_{18}O_4NCl$.—This salt is readily obtained when protopine (1 gram) is digested with freshly distilled phosphoryl chloride (3 c.c.). The alkaloid is sparingly soluble in the reagent and, on boiling, the white salt which is first produced partly dissolves and gradually gives place to a pale ochreous salt. After boiling for ten minutes, the excess of phosphoryl chloride is distilled off under diminished pressure from the steam-bath and the residue mixed with water, when the quaternary chloride separates as a voluminous mass of needles. This was collected, washed with dilute hydrochloric acid, and dissolved in just sufficient boiling water when, on standing, the salt separated as a mass of needles which were more definite than in the corresponding case of *iso*-cryptopine chloride (p. 883):

0·1402 gave 0·0541 AgCl. Cl = 9·5.

$C_{20}H_{18}O_4NCl$ requires Cl = 9·5 per cent.

iso*Protopine chloride* is a pale ochreous, satiny mass which darkens at 175°, is brick-red at 190°, and melts at 215° with effervescence to a black mass. It is very sparingly soluble in cold, and not readily so in boiling water, and the solution in acetic acid gives, with sulphuric acid, an immediate deep bluish-violet coloration.

iso*Protopine Disulphate*, $C_{20}H_{18}O_4N,HSO_4,H_2SO_4$.—This curious salt corresponds exactly with *iso*cryptopine disulphate (p. 884) and was prepared by adding the alkaloid (0·5 gram) to acetic acid (3 c.c.) and sulphuric acid (0·5 c.c.) and placing the test-tube containing the mixture in boiling water. The alkaloid rapidly dissolved, a brown solution was produced, and, after heating for an hour, the product was allowed to remain for two days in the ice-chest with occasional stirring, when it deposited a crystalline pre-

cipitate. This was collected, washed with acetic acid, dried in the steam-oven, and analysed:

0·3212 gave 0·2677 $BaSO_4$. S = 11·6.

$C_{20}H_{18}O_4N,HSO_4,H_2SO_4$ requires S = 12·0 per cent.

iso*Protopine disulphate* darkens somewhat at 180°, is red ochreous at 200°, then little further change takes place until 240°, when it becomes nearly black and melts at 247°, with evolution of gas, to a black froth. It is very sparingly soluble in cold water, but dissolves on boiling, and separates on keeping as a rather gelatinous mass consisting of groups of fine hairs. A trace of the salt dissolved in hot dilute sulphuric acid, gives a pink coloration on the addition of a little powdered manganese dioxide. The solution in acetic acid yields, on the addition of sulphuric acid, a fine bluish-violet coloration.

Like the corresponding *iso*cryptopine salt, a paste of the disulphate with a little water has the property of giving a blue streak when rubbed on a piece of polished black board. When ammonia is added to the hot aqueous solution of the disulphate, a yellow solution is produced and a very sparingly soluble, glistening precipitate separates, which is doubtless *iso*protopine sulphate, $(C_{20}H_{18}O_4N)_2SO_4$, since it has properties exactly resembling those of *iso*cryptopine sulphate (p. 886).

Anhydroprotopine. (Formula, p. 876).

This substance was obtained by boiling finely divided *iso*protopine chloride (0·5 gram) with methyl-alcoholic potassium hydroxide (3 c.c. of 25 per cent.), when decomposition rapidly took place and a lemon-yellow substance separated. After five minutes, water was added, the granular precipitate collected, washed with water, then with methyl alcohol, and dried on porous porcelain over phosphoric oxide. In this condition it melted at 60—65° and was not crystalline, but it rapidly became so in contact with warm methyl alcohol. It was dissolved as quickly as possible in boiling methyl alcohol, in which it is sparingly soluble, when the filtered solution deposited brilliant, pale yellow, well-developed prisms. The substance must not be dried in the water-oven because it rapidly darkens at about 90—95° and becomes a deep brown mass exactly as in the case of anhydrocryptopine (p. 975). When dried over phosphoric oxide until constant it yielded the following results:

0·1058 gave 0·2771 CO_2 and 0·0485 H_2O. C = 71·4; H = 5·1.

0·0993 „ 3·5 c.c. N_2 at 13° and 760 mm. N = 4·2.

$C_{20}H_{17}O_4N$ requires C = 71·6; H = 5·1; N = 4·2 per cent.

Anhydroprotopine melts at 114—115° and dissolves in mineral acids with a deep yellow colour, but it is a comparatively feeble base, since its solution in acetic acid is dissociated by water and the base

separates. The addition of sulphuric acid to the solution in glacial acetic acid produces an immediate port-wine coloration. It dissolves readily in concentrated hydrochloric acid, and the solution, on boiling, becomes red, but perhaps not quite so readily as in the case of anhydrocryptopine. After boiling for a minute, adding water, and stirring, a colourless, crystalline, rather slimy precipitate separates, which is sparingly soluble even in boiling water, and is probably the hydrochloride of *epi*protopine (compare *epi*cryptopine, p. 1008). The solution of the salt in much water gave, with ammonia, a nearly white base, the solution of which in ether had a pale blue fluorescence, and on concentrating and leaving for some days in the ice-chest a small, crystalline crust separated and the mother liquor on complete evaporation deposited an almost colourless, resinous base.

Anhydroprotopine dissolves in dilute hydrochloric acid (1 in 5), with some difficulty, to an almost colourless solution, and is reprecipitated unchanged on the addition of ammonia. When, however, the solution is heated on the steam-bath, anhydroprotopine behaves exactly like anhydrocryptopine in the same circumstances (compare p. 994), becomes at first deep yellow, then brown, and if, after about three minutes, the solution is cooled, it clouds and deposits a gum which crystallises on cooling. This hydrochloride closely resembles hydroxy*iso*anhydrodihydrocryptopine hydrochloride (*A*), it is sparingly soluble in water, crystallises readily, and the solution gives, on the addition of ammonia, a gelatinous precipitate of the base which, on warming, becomes granular.

The base dissolves readily in acetic acid and, on the addition of sulphuric acid, a pale yellow coloration is produced which, on keeping, becomes greenish-yellow, and in this colour reaction it differs somewhat from hydroxy*iso*anhydrodihydrocryptopine (*A*).

The Methylprotopines. (Formulæ, p. 876.)

The protopine methosulphate required for the preparation of these substances was obtained in the following manner (compare Danckwortt, *Habilitationsshrift*, Breslau, 1912, p. 45). Protopine (3 grams) was mixed with freshly distilled, neutral, methyl sulphate (6 c.c.), and, after remaining for twenty-four hours, the whole was heated in boiling water, when a clear solution was gradually produced, which soon commenced to deposit crystals. After remaining in the ice-chest for two days, the substance was collected, washed with methyl alcohol, and recrystallised from this solvent, from which it separated in curious bunches of prisms:

0·3227 gave 0·1452 $BaSO_4$. S = 6·2.

$C_{20}H_{19}O_5N,Me_2SO_4$ requires S = 6·6 per cent.

Protopine methosulphate becomes discoloured at 240° and melts at about 252° without effervescence to a yellow syrup; it is rather sparingly soluble in hot water and the solution gelatinises on cooling.

The hot aqueous solution gives no precipitate on the addition of ammonia.

Protopine Methiodide, $C_{20}H_{19}O_5N,MeI$.—The addition of potassium iodide to a hot aqueous solution of protopine methosulphate causes the separation of a viscid precipitate which on rubbing and warming soon becomes crystalline and very sparingly soluble in water.

When heated in a capillary tube this salt discoloured at about 210° and melted at 217° with effervescence to a yellow froth. It dissolves sparingly in boiling methyl alcohol, and separates in groups of stars or twin crystals:

0·1427 gave 0·0672 AgI. I = 25·5.

$C_{20}H_{19}O_5N,MeI$ requires I = 25·6 per cent.

When concentrated aqueous potassium hydroxide is added to a concentrated aqueous solution of protopine methosulphate there is no precipitate, but, on boiling, a milkiness is at once produced and a syrupy base separates, which is doubtless the γ-modification of methylprotopine (compare p. 1027), but it did not readily crystallise and was not further investigated. Danckwortt (*loc. cit.*, p. 46) also studied this decomposition, and was unable to isolate any crystalline substance from the syrupy product. Two crystalline methylprotopines, corresponding doubtless with the α- and γ-modifications of methylcryptopine (p. 961), may, however, be isolated from the product of the action of methyl-alcoholic potassium hydroxide on protopine methosulphate under the following conditions. Protopine methosulphate (3 grams) is intimately mixed with methyl-alcoholic potassium hydroxide (15 c.c. of 25 per cent.) and heated to boiling, when a yellow solution is produced, and after half an hour the bulk of the methyl alcohol is evaporated, water is added, and the syrupy, ochreous-coloured mass extracted with ether. The ethereal solution was thoroughly washed, dried over potassium carbonate, concentrated considerably, and left in the ice-chest for some days, but except for a slight crust nothing crystalline separated and, on evaporating the ether, a syrup remained which showed no signs of crystallising. When, however, this was rubbed with methyl alcohol and left for two days with the addition from time to time of small quantities of methyl alcohol, crystallisation was gradually induced and a chalky precipitate separated which was remarkably sparingly soluble in methyl alcohol and, when collected and washed with this solvent, was a colourless, crystalline powder.

The mother liquor gradually deposited a not inconsiderable, crystalline crust, and this was combined with the first crop. In this condition the substance softened at 108° and melted at about 130—135°, and when dissolved in boiling ethyl acetate and allowed to remain for some days a crust of well-developed, stout prisms of methylprotopine (α) separated:

0·1051 gave 0·2629 CO_2 and 0·0552 H_2O. C = 68·2; H = 5·8.

$C_{21}H_{21}O_5N$ requires C = 68·7; H = 5·7 per cent.

Methylprotopine (α) melts at 144—145° and is readily soluble in acetone, benzene, or chloroform, sparingly so in ether, and almost insoluble in light petroleum. The solution of the base in acetic acid gives, with sulphuric acid, an intense reddish-violet solution which, on the addition of a little water, becomes port-wine colour. It dissolves in concentrated hydrochloric acid to a colourless solution which, on warming, becomes yellow and almost immediately deep violet. The dilute solution of the hydrochloride gives with potassium iodide a caseous precipitate which melts under warm water and is readily soluble in methyl alcohol.

Methylprotopine (γ).—In order to isolate this substance, which is the principal product of the action of methyl-alcoholic potassium hydroxide on protopine methosulphate, the ethyl acetate mother liquors of the α-modification were concentrated somewhat and left in the ice-chest for several days, when a trace of the α-modification separated. The solution was then evaporated and the gum boiled with methyl alcohol, when a crystalline precipitate of methylprotopine (γ) separated as a granular powder*:

0·1043 gave 0·2618 CO_2 and 0·0554 H_2O. C = 68·5; H = 5·9.

0·1101 „ 3·5 c.c. N_2 at 13° and 764 mm. N = 3·7

$C_{21}H_{21}O_5N$ requires C = 68·7; H = 5·7; N = 3·8 per cent.

Methylprotopine (γ), obtained in this way, melted at 110—112°, but the fusion was not perfectly clear, so that it possibly contained a trace of the α-modification. It is readily soluble in benzene, acetone, or chloroform, rather sparingly so in ether, and very sparingly so in light petroleum. A trace of the substance dissolved in a drop of acetic acid gives, with sulphuric acid, a reddish-brown solution which becomes port-wine colour on the addition of two drops of water. The colourless solution in concentrated hydrochloric acid becomes yellow and then deep violet on boiling, and the addition of ammonia causes a pale ochreous precipitate to separate which, on warming, rapidly becomes crystalline.

The dilute solution of the hydrochloride gives, with potassium

* The methyl alcohol mother liquors from this yielded on evaporation only a very small quantity of a deep yellow dye, so that almost the whole of the methyl protopine had been obtained in a crystalline condition.

iodide, a caseous precipitate which immediately becomes crystalline; it has no definite melting point and on warming with water becomes viscid.

The Platinichloride.—This salt separates as a voluminous, gelatinous precipitate when platinic chloride is added to the cold dilute solution of the hydrochloride and, on warming, becomes crystalline:

0·3191 gave 0·0536 Pt. Pt = 16·7.

$(C_{21}H_{21}O_5N)_2,H_2PtCl_6$ requires Pt = 17·0 per cent.

It has no definite melting point, but becomes discoloured at about 180°, black at 210°, and decomposes with effervescence at about 230° to a black mass.

This research would have been impossible had it not been for the generosity of Messrs. T. and H. Smith, of Edinburgh, who undertook to collect the cryptopine from the mother liquors of the morphine manufacture and, during a number of years, supplied the author with considerable quantities of this rare alkaloid. The author wishes to thank the firm for their generosity, and also the managing director, Dr. Alexander Dey, for the interest he has always taken in the development of the research. All the substances described in this communication were prepared by the author himself, and he is therefore responsible for any inaccuracies, but most of the analyses were carried out with unusual skill by Mr. Fred Hall in the University Laboratory, Oxford.

The author has been fortunate during the last few years in having the valuable assistance of Professor Robert Robinson in discussing and disentangling the complicated changes as they were discovered, and he has also had valuable suggestions and criticism from Dr. F. L. Pyman and Dr. N. V. Sidgwick. The crystallographic measurements of some of the more characteristic derivatives of cryptopine have been kindly undertaken by Messrs. T. V. Barker, and A. Scott, and Miss M. V. Porter, and the author is greatly indebted to these for their work.

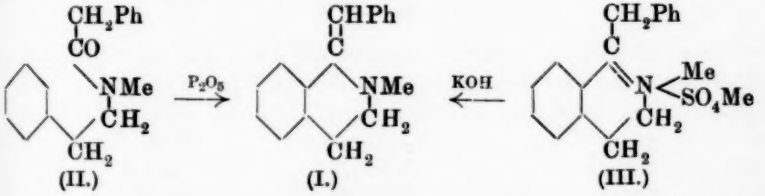
The author also wishes to state that much of the heavy expenditure connected with this investigation was defrayed by repeated grants from the Royal Society Research Fund.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD. [*Received, August 22nd,* 1916.]

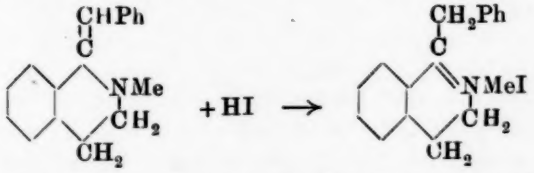
LXXII.—*An Extension of the Theory of Addition to Conjugated Unsaturated Systems. Part I. Note on the Constitution of the Salts of* 1-*Benzylidene*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline.

By Ellice Ettie Peden Hamilton and Robert Robinson.

During the course of synthetical experiments in the *iso*quinoline group the authors prepared the substance (I) named in the title by the dehydration of the *N*-phenylacetyl derivative (II) of *N*-methyl-β-phenylethylamine by means of phosphoric oxide in boiling xylene solution, and found that the same base was produced by the action of alkali hydroxides on the methochloride or methosulphate of 1-benzyl-3 : 4-dihydro*iso*quinoline (III):

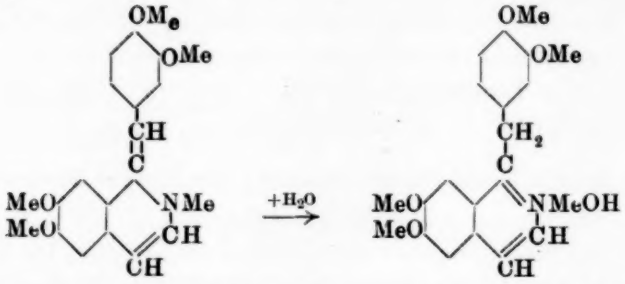


The investigation of this substance has been unavoidably interrupted, but will be resumed when opportunity occurs, and especially in connexion with the action of alkyl iodides on the compound and on other substances of similar type. In the formation of its salts, however, we have observed a reaction of an interesting character, since no difference can be detected between the salts of the base obtained normally and the corresponding metho-salts of 1-benzyl-3 : 4-dihydro*iso*quinoline. The constitution of the latter class of substance is almost certainly normal, so that the formation of the salts of the benzylidene base involves the change:

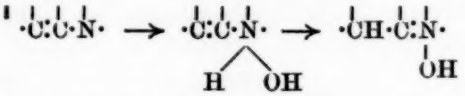


Similar reactions have been previously discussed by Decker and Klauser (*Ber.*, 1904, **37**, 523) and by Decker (*Ber.*, 1905, **38**, 2893). Decker and Klauser were able to show that *N*-methyl*iso*papaverine reacts with water to form papaverine methyl hydroxide and with acids to form the papaverine metho-salts. The former reaction

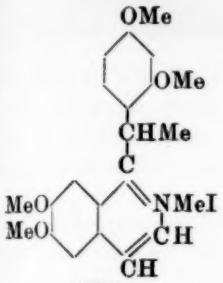
is illustrated below, and is typical of all the cases examined by Decker:



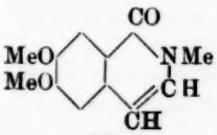
In discussing the mechanism of the reaction, Decker and Klauser suggest the scheme:



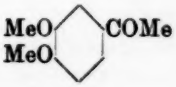
but mention without further comment the possibility that the latent valencies of the tervalent nitrogen are conjugated with the ethylene linking, and that the addition may then be explained by an application of Thiele's theory (*Annalen*, 1899, **306**, 87). In a later and important paper Decker (*loc. cit.*) emphasises the latter theory of the reactions, and multiplies the number of instances in which such an assumption of conjugation may be made. In all these examples of the formation of ammonium, oxonium, or sulphonium salts, however, the substance produced is of true aromatic type, and in view of the tendency to produce compounds of benzenoid character it cannot be claimed that the evidence adduced was sufficient to eliminate the scheme of direct addition, followed by migration of a hydrogen atom and the change of position of an ethylene linking. In the example of this type of reaction which we have noted, the substance produced is not of aromatic type, and in the succeeding communication the formation of salts of unsaturated bases of the aliphatic series is shown to involve the change in position of the ethylene linking. The greatest support to the theory of the conjugated system nitrogen–ethylene linking is, however, derived from the observation that *C*-alkylation results when alkyl haloids unite with bases containing such a system. This point also is developed in the paper which follows, but we have found that at least one of the products of the action of methyl iodide on *N*-methyl*iso*papaverine is the methiodide (IV), since the corresponding quaternary hydroxide yields on oxidation with potassium permanganate dimethoxy-*N*-methyl*iso*quinolone (V) and acetoveratrone (VI):



(IV.)

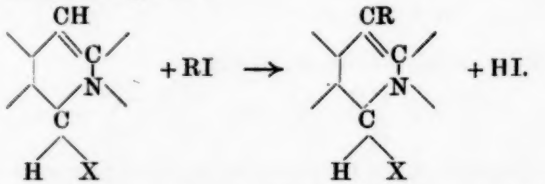


(V.)

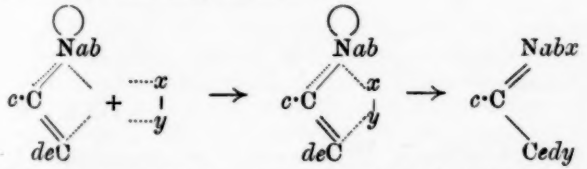


(VI,)

Similar *C*-alkylations have been observed by Freund and Fleischer (*Annalen*, 1915, **409**, 188) in the dihydroberberine series, but these authors hold the view that the observed reactions are due to a "reactive hydrogen atom," and, writing a part only of the structures, the mechanism given is:



The authors, however, consider that all these alkylations on the carbon atom give the most definite support to the theory of the divided addition to a conjugated system comprising an ethylene linking and a tervalent nitrogen atom, and represent all these processes in the following manner:



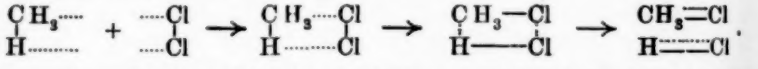
It will be observed that in order to make the Thiele explanation of divided additions to conjugated systems applicable to the case under discussion, it is necessary to assume that the tervalent nitrogen atom possesses two units of partial valency, and these should not be confused with the latent valencies of tervalent nitrogen. Probably the logical assumption is that a unit of partial or residual valency accompanies each normal or latent valency, so that the following symbols should represent the carbon and tervalent nitrogen atoms:

The expression , however, may be employed, since it is clearly unnecessary to symbolise the residual affinity which is saturated along with the normal valencies to which it appertains, and which is neither disturbed by the conjugation nor need be represented to enable us to locate the reactive centres in the molecule.

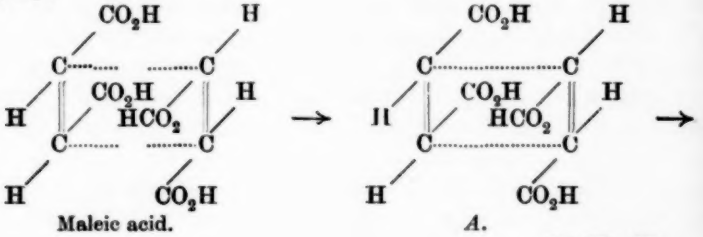
The actual process of addition is represented as a cohesion by means of the partial valencies, and this is followed by a movement*

* In general agreement with the theory of chemical reactivity advocated by Baly (*J. Amer. Chem. Soc.*, 1915, **37**, 981—982), it seems probable that such movements are the characteristic feature of all chemical reactions resulting in formation of stable additive products, or which are formally represented as substitutions or decompositions. It will be necessary to assume the disruption of partial valencies connecting two atoms as well as the possibility of combination by residual affinity. The following examples of the representation of reactions on these lines may be appended:

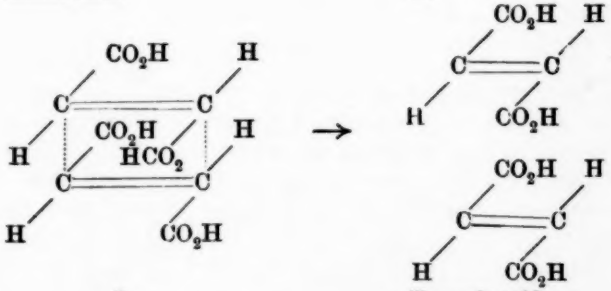
Kekulé's theory of the chlorination of methane:



Stewart's explanation of the transmutation of ethylene isomerides (P., 1905, **21**, 73):



Maleic acid. *A.*



B. Fumaric acid.

In this case the change from *A* to *B*, which involves the alteration in position of electrons, need not pass through the stage of *cyclo*butane-tetracarboxylic acid.

It is in connexion with molecular rearrangement and migration that the

of electrons along potential gradients. The reactive centres to which addition occurs will be determined mainly by the effects of conjugation, although in facilitating these reactions the stereochemical considerations advanced by Perkin and Robinson (T., 1908, **93**, 1097) may have some part, especially as the initial formation of a five-membered ring has been assumed.

Experimental.

Piperonylidene-β-phenylethylamine, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

Piperonal (68 grams) was mixed with β-phenylethylamine (50 grams) when, after the considerable cooling due to the solution of the solid, the temperature began to rise and was kept below 50°. The mass soon become completely solid, and, for the purposes of the preparation of *N*-methyl-β-phenylethylamine, was dried at 100° in a vacuum. A specimen was crystallised from alcohol, and obtained in fan-shaped aggregates of needles or as lustrous, oblong prisms melting at 68—69°:

0·1670 gave 0·4642 CO_2 and 0·0882 H_2O. C = 75·8; H = 5·9.

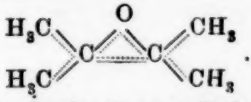
$C_{16}H_{15}O_2N$ requires C = 75·9; H = 5·9 per cent.

This condensation product is easily resolved into its components on warming with dilute hydrochloric acid.

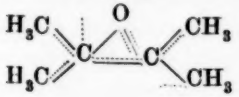
Preparation of N-*Methyl-β-phenylethylamine.*

The method employed for the preparation of this amine is based on a process originally devised by Forster (T., 1899, **75**, 936), and

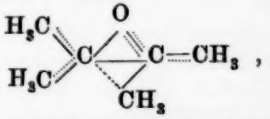
advantage of the expression of all the partial valencies, or what may be called the unsaturation of the single bond, becomes most apparent, since the authors have become convinced tnat the majority, if not all, such changes are best explained by the assumption of preliminary ring-formation with the aid of partial valency. The pinacone-pinacolin change may be cited as an example. Accepting the theory that the pinacone first loses water with the formation of an oxide, the latter substance will be represented as:



Conjugation of the partial valencies then results in the stages



and



and the same condition may obviously be reached by three other similar routes. The last stage already has the same atomic arrangement as pinacolin, which is reached by a movement of electrons.

used for the preparation of pure secondary bornylamines. A primary amine is condensed with an aldehyde, and the resulting azomethine converted into a quaternary salt by the action of an alkyl haloid. This salt is then decomposed by water, and the hydriodide of a secondary amine and the original aldehyde are the products.

Decker and Becker (*Annalen*, 1913, **395**, 362) have prepared a number of secondary amines by this method, although in their paper they do not refer to the work of Forster. They obtained *N*-methyl-β-phenylethylamine by decomposing the methiodide of benzylidenephenylethylamine with aqueous alcohol, but our experiments, using the piperonylidene compound, were in progress at the time of publication of the investigations of Decker and Becker, and apart from this the use of piperonal has certain advantages in that the methiodides are more readily formed, and are usually crystalline substances. The dried piperonylidene-β-phenylethylamine was dissolved in an excess of methyl iodide and the solution allowed to remain at the room temperature. The methiodide gradually separated, and the reaction was complete after about three weeks. The yellow crystals were flat needles, and the substance can be crystallised from alcohol, but even when alcohol dried over calcium was employed the percentage of iodine was found to vary with different specimens, indicating decomposition. The substance was therefore usually employed directly after washing with ether. On decomposition with warm water piperonal and *N*-methylphenylethylamine hydriodide resulted. The piperonal was removed by extraction with ether, and the aqueous solution basified. The amine was extracted, converted into hydrochloride, and this derivative crystallised from a mixture of alcohol and ether. It melted as described by Decker and Becker (*loc. cit.*) at 155—157°.

N-*Phenylacetyl*-N-*methyl*-β-*phenylethylamine* (Formula II).

Piperonylidene-β-phenylethylamine methiodide (40 grams) was decomposed by warming with water (200 c.c.), the cooled solution extracted with ether, and the aqueous solution separated. A solution of potassium hydroxide (20 grams) in water (50 c.c.) was then added and, with vigorous stirring and cooling, phenylacetyl chloride (25 grams). When the odour of the acid chloride was no longer observed the oil was dissolved in ether, and the extract dried, and distilled. At a pressure of 20 mm. the product of the reaction distilled without decomposition at 235°. The colourless, viscid substance was not obtained in the crystalline condition:

0·2055 gave 0·6063 CO_2 and 0·1363 H_2O. C = 80·4; H = 7·4.

$C_{17}H_{19}ON$ requires C = 80·6; H = 7·5 per cent.

1 *Benzylidene-2-methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (Formula I).

This base is most conveniently obtained by treating 1-benzyl-3 : 4-dihydro*iso*quinoline with a little more than a molecular proportion of pure methyl sulphate in benzene solution and, after removing the benzene by distillation, dissolving the product in water and basifying with potassium hydroxide. The oil which separates is then extracted and distilled as described in the following method of preparation. The amide described in the last section was dissolved in six times its weight of xylene and three times its weight of phosphoric oxide added. The mixture was heated at the point of incipient ebullition in an oil-bath during an hour, cooled, and treated with water. The aqueous layer was separated, and some adhering xylene removed by ether. The acid solution was then rendered strongly alkaline and extracted with ether, the ethereal solution being then dried by solid potassium hydroxide and distilled, finally in a vacuum. The base passed over as a golden-yellow syrup, and boiled constantly at 213°/21 mm.:

0·1381 gave 0·4379 CO_2 and 0·0910 H_2O. C = 86·5; H = 7·3.
$C_{17}H_{17}N$ requires C = 86·8; H = 7·2 per cent.

The yellow colour of the base is characteristic, and does not appear to be due to impurity. As stated in the introduction, the examination of this base is not complete, but a careful comparison has been made between specimens of its salts which can be obtained on the one hand from the base itself with the corresponding acid, or, on the other, from 1-benzyl-3 : 4-dihydro*iso*quinoline by means of an alkyl haloid or by double decomposition from these additive products.

The Hydriodide.—This was obtained by the addition of potassium iodide to a solution of the benzylidene base in dilute sulphuric acid, as well as by the addition of methyl iodide to benzyldihydro*iso*-quinoline. The two products were completely identical. It crystallises from alcohol in pale yellow, hexagonal tablets, and melts and decomposes at 196—198°.

The Aurichloride.—A solution of the hydrochloride was obtained direct from the base and also by treatment of the methiodide of benzyldihydro*iso*quinoline with silver chloride in aqueous solution, and further by the addition of hydrochloric acid to a solution of the methosulphate of the latter base. On the addition of gold chloride the same aurichloride was precipitated in each case, and the identity was proved by comparison and by the method of melting points of mixtures. This aurichloride is sparingly soluble in water, but may be crystallised from ethyl alcohol and obtained

in orange needles with sharp points and serrated edges. It melts at 135—137°, apparently without decomposition:

0·4230 gave 0·1442 Au. Au = 34·1.

$C_{17}H_{17}N,HAuCl_4$ requires Au = 34·3 per cent.

The Platinichloride.—This derivative was obtained by the addition of platinic chloride to the solution of the hydrochloride obtained by the three methods described above. In each case the same substance was produced, and the melting points of mixtures of the specimens showed no depression. The substance is obtained as a buff precipitate, very sparingly soluble in most solvents, but it can be conveniently crystallised from formic acid (D 1·2). It is obtained in aggregates of orange-yellow prisms melting and decomposing at 215—216°:

0·5335 gave 0·1174 Pt. Pt = 22·0.

$(C_{17}H_{17}N)_2H_2PtCl_6$ requires Pt = 22·2 per cent.

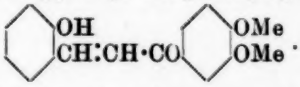
C-*Alkylation of* N-*Methyl*iso*papaverine.*

N-Methyl*iso*papaverine (Decker and Klauser, *loc. cit.*) (20 grams) was gently boiled during five hours with methyl iodide (50 grams), and the excess of the iodide then removed by distillation, and finally by a current of air. The yellowish-brown, viscid residue was heated on the steam-bath with water (1000 c.c.), and an excess of silver chloride, and the pale yellow solution separated from the precipitate of mixed silver chloride and iodide. Benzene and an excess of potassium hydroxide were added, and the yellow base produced was dissolved in the benzene, which was separated, dried with potassium hydroxide, and the solvent removed from the filtered liquid by distillation. The residue could not be crystallised, so it was dissolved in water, mixed with a large volume of benzene, and then oxidised by the addition of 2 per cent. aqueous potassium permanganate at the ordinary temperature and with continual stirring until the pink colour was no longer quickly discharged. The whole was then heated to the boiling point of benzene, and filtered. The benzene extract was separated, and extracted with small quantities of concentrated hydrochloric acid. The colourless crystals which separated were mixed with the acid solution (*A*). The benzene solution was then washed with water, dried with calcium chloride, and evaporated. The residual oil had the properties of acetoveratrone, and did not appear to contain veratraldehyde. It may, however, have contained some nitrogenous impurities, and it was found difficult to prepare the semicarbazone. The condensation product with salicylaldehyde was therefore prepared from the oil in the manner described in the next section, and this showed the correct melting point and unde-

pressed mixed melting points. The oxonium ferrichloride was also made as described below, since this derivative is highly characteristic.

(*A*) was diluted with water and mixed with an aqueous solution of picric acid. The yellow precipitate was collected, dissolved in ethyl alcohol, and water added until a faint turbidity was produced when still warm. On cooling, a picrate separated in crystals, and was recrystallised from alcohol. It melted at about 135°, and the base contained was regenerated by means of a dilute solution of ammonia and dissolved in ether. The ethereal solution was separated, dried, and evaporated, leaving an oil which soon crystallised. The substance was recrystallised from benzene, and obtained in prisms melting at 107—109°, and at the same temperature when mixed with a specimen of dimethoxy-*N*-methyl*iso*quinolone obtained by the oxidation of papaverine methosulphate (Decker, Einbeck, Koch, and Pschorr, *Ber.*, 1904, **37**, 3396).

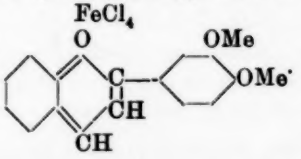
3 : 4-*Dimethoxyphenyl* 2-*Hydroxystyryl Ketone*,



Salicylaldehyde (20 grams) and acetoveratrone (26 grams) were dissolved in methyl alcohol (50 c.c.) and heated to boiling, after which potassium hydroxide (100 c.c. of 20 per cent.) was added, and the mixture allowed to remain during a week at the ordinary temperature. The brick-red potassium salt of the unsaturated ketone was gradually formed, and was separated and washed with a little 10 per cent. aqueous potassium hydroxide. It was recrystallised from a mixture of alcohol and ether, and then dissolved in hot water and exactly decomposed with acetic acid. The oily precipitate was kneaded with ice-water, and soon crystallised. On recrystallisation from methyl alcohol it was obtained in bright yellow, prismatic needles melting at 153° with decomposition to a green liquid :

0·1322 gave 0·3473 CO_2 and 0·0700 H_2O. C = 71·6; H = 5·9.
$C_{17}H_{16}O_4$ requires C = 71·8; H = 5·6 per cent.

3′ : 4′-*Dimethoxy*-2-*phenyl*-1 : 4-*benzopyranol Anhydroferrichloride*,



The foregoing unsaturated ketone was dissolved in hot hydrochloric acid, and the solution boiled for five minutes, diluted with

water, and filtered. The orange-red solution of the oxonium salt was mixed with an excess of ferric chloride, and the brown precipitate collected and crystallised from glacial acetic acid, in which the substance is sparingly soluble. Chocolate-brown needles with beetle-green reflex were obtained and dried at 100°:

0·1743 gave 0·2823 CO_2 and 0·0535 H_2O. C = 44·2; H = 3·4.
$C_{17}H_{15}O_3,FeCl_4$ requires C = 43·9; H = 3·2 per cent.

The substance melts at 201°, and is readily soluble in water to an orange-red solution.

UNIVERSITY OF SYDNEY,
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[*Received, August 25th*, 1916.]

LXXIII.—*An Extension of the Theory of Addition to Conjugated Unsaturated Systems. Part II. The C-Alkylation of Certain Derivatives of β-Aminocrotonic Acid and the Mechanism of the Alkylation of Ethyl Acetoacetate and Similar Substances.*

By ROBERT ROBINSON.

IN Part I. it has been indicated that the formation of salts and additive products with alkyl haloids of an unsaturated base of the *iso*quinoline group follows such a course that the latent affinities of the tervalent nitrogen atom must be assumed to be conjugated with an ethylene linking, and in the present communication the similar behaviour of unsaturated bases of the aliphatic series is noted.

In the first place, it may be pointed out that the ready hydrolysis of ethyl β-aminocrotonate and its derivatives in acid solution is probably due to the alteration in position of the double linking during the formation of the salt. True enamic salts, such as aniline hydrochloride, are not hydrolysed very readily, whereas it is well known that salts of enimic constitution are easily resolved by water into an ammonium salt and a carbonyl compound. Thus the ketimine salts, the imine-ether hydrochlorides, and the additive products between azomethine bases and alkyl haloids are all readily decomposed by water, as shown below:

$$CMe_2{:}NH + HCl + H_2O \longrightarrow CMe_2{:}O + NH_4Cl.$$
$$OH{\cdot}CHPh{\cdot}C(OMe){:}NH_2Cl + H_2O \longrightarrow OH{\cdot}CHPh{\cdot}CO_2Me + NH_4Cl.$$
$$CHPh{:}NMe_2I + H_2O \longrightarrow CHPhO + NH_2Me_2I.$$

It is reasonable therefore to attribute the ease with which ethyl β-aminocrotonate is hydrolysed to the reactions:

$$NH_2\cdot CMe{:}CH\cdot CO_2Et + HCl \longrightarrow NH_2Cl{:}CMe\cdot CH_2\cdot CO_2Et + H_2O \longrightarrow O{:}CMe\cdot CH_2\cdot CO_2Et + NH_4Cl.$$

So long ago as 1883, Collie (*Annalen*, **226**, 316) studied the action of ethyl iodide on ethyl β-aminocrotonate, and after the addition of ether, evidently moist, obtained ammonium iodide and ethyl α-acetylbutyrate as the products of the reaction. The result is clearly to be explained in the following manner:

$$NH_2\cdot CMe{:}CH\cdot CO_2Et + EtI \longrightarrow NH_2I{:}CMe\cdot CHEt\cdot CO_2Et \longrightarrow O{:}CMe\cdot CHEt\cdot CO_2Et + NH_4I.$$

However, Conrad and Epstein (*Ber.*, 1887, **20**, 3055) showed that ethyl β-aminocrotonate dissolved an atomic proportion of sodium in ethereal solution with the formation of a sodium compund, and on the addition of methyl iodide the ensuing reaction resulted in the production of sodium iodide and ethyl β-amino-α-methylcrotonate. It would have been possible to argue from this that the alkylation of the aminocrotonic ester was occasioned solely by the capacity of this substance to form a sodium compound, and Collie's reaction could then be explained by imagining the base to unite with water to form a substituted ammonium hydroxide the positive radicle of which functions as an atom of an alkali metal and displaces hydrogen from another molecule of the ester. In order to dispose of this view the author has studied the behaviour of ethyl β-diethylaminocrotonate with methyl and ethyl iodides. This ester is quite inactive towards sodium, and yet its additive products with the alkyl haloids named yield, on decomposition with water, diethylamine hydriodide and ethyl α-acetylpropionate and ethyl α-acetylbutyrate respectively. The production of the former substance is represented as follows:

$$NEt_2\cdot CMe{:}CH\cdot CO_2Et + MeI \longrightarrow NEt_2I{:}CMe\cdot CHMe\cdot CO_2Et + H_2O \longrightarrow O{:}CMe\cdot CHMe\cdot CO_2Et + NH_2Et_2I.$$

Conrad and Epstein's sodium compound is probably a sodamide derivative, and the reaction with methyl iodide will fit into the general scheme, as illustrated below:

$$NHNa\cdot CMe{:}CH\cdot CO_2Et + MeI \longrightarrow NHNaI{:}CMe\cdot CHMe\cdot CO_2Et \longrightarrow NaI + NH{:}CMe\cdot CHMe\cdot CO_2Et \longrightarrow NH_2\cdot CMe{:}CHMe\cdot CO_2Et.$$

From the point of view adopted it was important to realise experimentally the introduction of an alkyl group by these additive reactions to a carbon atom not itself joined to hydrogen. Such a reaction, which is to be expected on the theory of the conjugated nitrogen–ethylene linking system, would be quite incompatible with the hypothesis of the reactive hydrogen atom. Accordingly, the crystalline dimethyl ethylenebis-β-amino-α-methylcrotonate was prepared by the condensation of ethylenediamine and methyl α-acetylpropionate, and after treatment with methyl iodide and decomposition with water, methyl α-acetyl*iso*butyrate was obtained. In this case the main product was contaminated with other substances of undetermined nature, but it is clear that an explanation of the production of the dialkylated acetoacetic ester must be on the following lines:

$$CO_2Me\cdot CMe{:}CMe\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot CMe{:}CMe\cdot CO_2Me + 2MeI \longrightarrow$$
$$CO_2Me\cdot CMe_2\cdot CMe{:}NHI\cdot CH_2\cdot CH_2\cdot NHI{:}CMe\cdot CMe_2\cdot CO_2Me +$$
$$2H_2O \longrightarrow CO_2Me\cdot CMe_2\cdot COMe + NH_3I\cdot CH_2\cdot CH_2\cdot NH_3I +$$
$$COMe\cdot CMe_2\cdot CO_2Me.$$

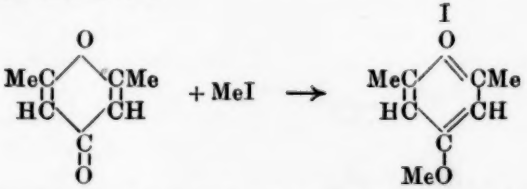
It appears an obvious extension of the theory to assume that unsaturated elements other than nitrogen can be conjugated with ethylene linkings or other unsaturated centres, and the mechanism of many reactions probably involves addition to such systems. The analogy between the cases already discussed and the alkylation of ethyl acetoacetate by the usual method will be apparent. The addition theory for this reaction has been viewed with some suspicion, mainly because there was no clear analogy for the assumption of the addition of alkyl haloids to an ethylene linking. This analogy is now forthcoming, and the mechanism advocated is shown below, and may be compared with that given for the action of ethyl iodide on ethyl β-aminocrotonate:

$$ONa\cdot CMe{:}CH\cdot CO_2Et + MeI \longrightarrow$$
$$NaIO{:}CMe\cdot CHMe\cdot CO_2Et \longrightarrow$$
$$COMe\cdot CHMe\cdot CO_2Et + NaI.$$

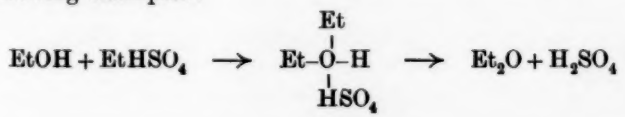
$$ONa\cdot CMe{:}CMe\cdot CO_2Et + MeI \longrightarrow ,$$
$$NaIO{:}CMe\cdot CMe_2\cdot CO_2Et \longrightarrow$$
$$COMe\cdot CMe_2\cdot CO_2Et + NaI.$$

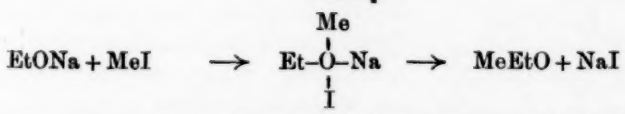
Since sodium enolates undergo alkylation, whereas the free enols as a general rule do not, it is necessary to assume that the unsaturated character of the oxygen atom is increased by its union with a highly positive atom such as sodium. Direct proof is unobtainable, but the behaviour of the nitrogen atom furnishes an analogy which indicates that the assumption is a fair one. It is, of course, well established that the tendency of nitrogen to pass into the quinquevalent condition is increased by union with the more positive

groups, whilst this tendency may be almost extinguished when the groups or atoms attached to the nitrogen atom are of strongly negative character. There is reason to suppose, therefore, that the oxygen atom would be more basic when united to sodium than in a simple hydroxy-derivative. This conclusion is not, in the author's opinion, invalidated by the observation which has frequently been made, that oxonium salts are more readily produced from substances of the type ·O·CH:CH· than from substances of the type ·O·CH_2·CH_2·, which are in other respects of similar constitution. This is probably due to the conjugation of the oxygen with the unsaturated system. Proof has been furnished by Baeyer (*Ber.*, 1910, **43**, 2337) that dimethylpyrone methiodide is a methoxy-compound, and the reaction which is involved in its formation is one of addition to the conjugated system ·O·C:C·C:O. This process is represented as follows:



The acceptance of this theory of the mechanism of alkylation of such substances as ethyl acetoacetate would give support to the idea that simple ether syntheses were also due to additions, as shown in the following examples:





Experience has shown that for the occurrence of the divided addition to conjugated systems of ethylene linkings a certain balance in the unsaturation of the two centres is requisite.

Thus addition does not always follow the course:

$$a=b-c=d+A\,.\,B \longrightarrow A-a-b=c-d-B,$$

but sometimes:

$$a=b-c=d+A\,.\,B \longrightarrow A-a-bB\,.\,c=d.$$

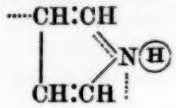
Parallel cases in the conjugated systems now under discussion would be the formation of the hydrochloride, ·CH:CH·N$\begin{matrix}H\\Cl\end{matrix}$,

from $\cdot CH{:}CH\cdot \underset{|}{N}$, or the production of an *O*-ether in the reaction between a sodium enolate and an alkyl iodide. In such cases the conjugation has broken down, and the more unsaturated of the two groups has reacted by itself. The circumstances which cause this behaviour may be connected with the conditions of the reaction or with the constitution of either the unsaturated substance or the compound added to it, and it will be clear that a very complicated problem is presented by every case. Possibly silver enolates yield with alkyl iodides the *O*-derivatives mainly because the silver atom itself is unsaturated and attracts the alkyl iodide, but the whole subject cannot be further discussed at the present time.

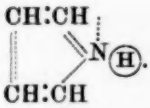
Among the many developments of an extended theory of conjugated unsaturated centres the following are the most interesting, and the author hopes to deal with them in due course.

(I) The reactions of aromatic amines and phenols, especially those in which nucleus substitution occurs with far greater readiness than in the parent from which the amine or phenol is derived, must probably be ascribed to additions to a conjugated system which includes the nitrogen or oxygen atoms.

(II) In a similar manner the reactivity of certain heterocyclic substances may receive an explanation. Pyrrole, for example, contains the conjugated systems:



and

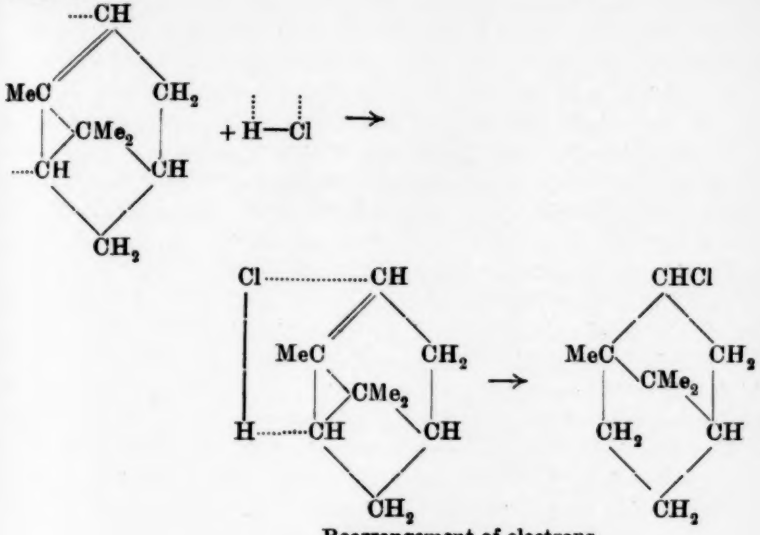


addition to which involves substitution in the β- and α-positions respectively.

(III) Addition to conjugated systems is probably a reversible process. Decomposition with formation of a conjugated system is a stage in the reactions which could be discussed under (I) and (II), and such decompositions are much in evidence in the transition of benzenoid to quinonoid types. They also afford an explanation of the direction of decomposition of per-methylated *cyclo*ammonium hydroxides.

(IV) The definition of an unsaturated system may be widely extended. As one example from many possibilities, the unsaturation of *cyclo*propane and *cyclo*butane rings may be cited. Substances containing these structures frequently absorb the elements of halogen acids. Many curious changes, notably in the terpene group, receive an explanation by assuming a divided addition to a conjugated system comprising an ethylene linking and an unsaturated ring. An example of this may be adduced in the production

of pinene hydrochloride, which would be expressed in the following stages:



Rearrangement of electrons.

EXPERIMENTAL.

Action of Methyl Iodide on Ethyl β-Diethylaminocrotonate.

Ethyl β-diethylaminocrotonate (Kuckert, *Ber.*, 1885, **18**, 618) is a weak base which dissolves in dilute hydrochloric acid and can be recovered on the addition of sodium hydroxide. It is therefore not so readily hydrolysed as the majority of substances of similar constitution. If the solution is allowed to remain or is heated, hydrolysis results in the formation of diethylamine and, in the first place, of ethyl acetoacetate. In faintly acid solution the substance condenses with diazonium salts, with the formation of orange-yellow to red azo-compounds. The ester is completely inactive towards sodium, which remains untarnished even when melted under the pure substance. It combines with alkyl haloids with some difficulty, and it is advisable to employ an excess of the iodide and an elevated temperature, but it was found that the reaction with methyl iodide proceeds slowly to completion at the ordinary temperature and with the employment of equimolecular proportions of the reacting substances.

Ethyl β-diethylaminocrotonate (30 grams) was mixed with methyl iodide (25 grams) and the clear liquid allowed to remain at the ordinary temperature. The next day it was found that two layers had separated, and on further keeping the upper layer increased

in volume until after about twenty days the lower layer had disappeared. The viscid, oily additive product could not be crystallised, and was decomposed by warming on the steam-bath with water (100 c.c.). The oil which separated was dissolved in ether, the ethereal solution washed with dilute hydrochloric acid and with water, dried, and distilled. After the removal of the solvent almost the whole distilled at 184—190° and consisted of ethyl α-acetylpropionate. The first drops of this fraction gave the ferric chloride coloration characteristic of monoalkylated acetoacetic esters, being much bluer than with ethyl acetoacetate itself, whilst the last drops were completely soluble in aqueous potassium hydroxide, and did not contain, therefore, the dialkylated derivative. For further identification, a portion of the oil was hydrolysed by dilute sulphuric acid, and the resulting methyl ethyl ketone identified as the semicarbazone which melted at 148°. This is 4° higher than the recorded melting point, but a specimen of the semicarbazone made from pure methyl ethyl ketone also melted at 148°.

Exactly similar results were obtained when the additive product was prepared by boiling a solution of the basic ester in excess of methyl iodide during twenty-four hours.

Action of Ethyl Iodide on Ethyl β-Diethylaminocrotonate.

In this case the reaction was impracticably slow at the ordinary temperature, and the ester was boiled during fifty hours with four times its volume of ethyl iodide. As in the previous example, the additive product separated as a viscous layer above the excess of the iodide. After removing unchanged ethyl iodide by distillation from the steam-bath and by a current of air, the product (from 40 grams of ester) was decomposed by heating on the steam-bath during ten minutes with water (150 c.c.), cooled, mixed with dilute hydrochloric acid, and extracted with ether. After removal of the solvent from the dried solution the residue was distilled, and passed over between 170° and 200°, the fractions below 194° and above 196° being relatively small. In this case also it appears that the unchanged ethyl acetoacetate and dialkylated ester are absent, or present in but small relative amount. The fraction boiling at 195° consisted of almost pure ethyl α-acetylbutyrate, and was hydrolysed to methyl propyl ketone by boiling with dilute sulphuric acid. The ketone was separated and distilled constantly at 101°, whilst its semicarbazone melted at 111°.

The acid solution from which the ester was extracted was boiled and concentrated. It was then cooled, rendered strongly alkaline by the addition of an excess of powdered sodium hydroxide, and the base which separated was extracted with ether. The solution

was dried with potassium hydroxide and fractionated, using an efficient column. After fractions consisting of ether and a mixture of ether and diethylamine, pure diethylamine distilled at 55—56°. When the temperature of the vapour reached 65° a small residue was left in the flask. This was dissolved in dilute hydrochloric acid, a solution of sodium nitrite added, and the liquid extracted with ether, and the separated aqueous layer concentrated, cooled, rendered strongly alkaline, and again extracted with ether. After drying with potassium hydroxide the ether was removed by cautious distillation, and examination of the inconsiderable residue showed it to consist of triethylamine. The hydrobromide melted at 250°.

This result indicates that only a small proportion of the ethyl iodide is added directly to the nitrogen. It is hoped that an opportunity may soon occur to institute experiments of a quantitative character in order to determine the ratio of the addition to the conjugated system and to the nitrogen alone under various conditions and with different alkyl haloids, as a comparison of these reactions with that between alkyl haloids and ethyl sodioacetoacetate and similar substances cannot fail to bring to light similarities or divergences which would present interesting features.

Dimethyl Ethylenebis-β-amino-α-methylcrotonate,
$CO_2Me{\cdot}CMe{:}CMe{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CMe{:}CMe{\cdot}CO_2Me$.

It was desired to realise a *C*-alkylation of a β-aminocrotonic ester in a case where there is no hydrogen atom attached to the carbon which is to be alkylated, and an attempt was accordingly made to prepare methyl β-diethylamino-α-methylcrotonate by the condensation of diethylamine and methyl α-acetylpropionate. After allowing the substances to remain mixed together during ten days there was no evidence of reaction, and the liquid was separated into the original components by fractional distillation. Mason and Dryfoos (T., 1893, **63**, 1310) have obtained crystalline condensation products from substituted acetoacetic esters and ethylenediamine, and a similar product was therefore prepared from methyl α-acetylpropionate. The ester (52 grams) was dissolved in methyl alcohol (50 c.c.), mixed with ethylenediamine hydrate (12 grams), and the liquid boiled during fifteen minutes and then allowed to cool. The crystals which separated were collected and recrystallised from methyl alcohol, being so obtained in pearly leaflets melting at 126°:

0·1438 gave 0·3125 CO_2. C = 59·3.

$C_{14}H_{24}O_4N_2$ requires C = 59·1 per cent.

The substance is readily soluble in most organic solvents. It is comparatively stable towards alkaline solutions, but is rapidly

hydrolysed in dilute acid solution with the formation of the original components. The reaction with methyl iodide was examined and found to proceed to a considerable extent in the expected direction, but in this case by-products of undetermined nature were also formed. The pure dry base (10 grams) was dissolved in methyl iodide (50 c.c.), and the mixture allowed to remain overnight and then boiled during eight hours. The excess of methyl iodide was removed by distillation, the residue decomposed by warm dilute hydrochloric acid, and extracted with ether. The ethereal solution was washed with aqueous potassium hydroxide to remove enols, and this process often repeated, as it was found that the colourless ethereal solution contained a substance which dissolved in the alkaline solution with a bright yellow colour. The solution was dried and distilled, and the fraction between 172° and 176° was found to consist of methyl α-acetyl*iso*butyrate. It gave no colour with ferric chloride in alcoholic solution, had a strong peppermint odour, and on hydrolysis with boiling dilute sulphuric acid gave rise to methyl *iso*propyl ketone, the semicarbazone of which crystallised from a dilute salt solution in needles melting at 114°. The methyl acetyl*iso*butyrate constituted perhaps two-thirds of the oil insoluble in potassium hydroxide, and the remainder of the product was of much higher boiling point and has not yet been examined.

UNIVERSITY OF LIVERPOOL. [*Received, August 25th*, 1916.]

LXXIV.—*The Functions of the Higher Valencies.*

By ARTHUR CLAYTON.

ONE of the most noticeable features of the periodic classification of the elements is the connexion between valency and atomic weight. As is well known, the constitution of the higher oxides shows that valency rises regularly throughout the groups, whilst the composition of the hydrides indicates a rise to a maximum in the fourth group followed by a decline to zero in the eighth. In view of the complete development of oxygen valency, the question arises as to the cause of this peculiar variation of hydrogen valency, which follows so regular a path that it seems some definite explanation should be forthcoming.

Clearly the phenomenon must be due to some property of (*a*) the hydrogen atoms, or (*b*) the atoms to which they are united. Taking the two cases in order:

(*a*) The decline of hydrogen valency cannot be due to any property peculiar to the hydrogen atom, because the alkides are of

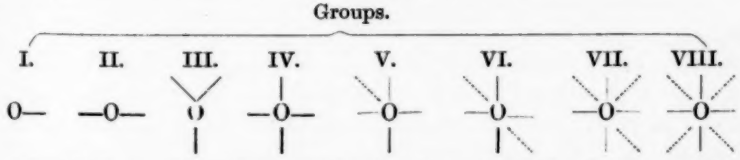
similar constitution in this respect to the hydrides. Nor can it be due to the electropositive nature of hydrogen, for the decline is co-existent with an increase in electronegative character. Finally, the phenomenon cannot be explained by assuming the existence of some undefinable property of the hydrogen atom which prohibits the attachment of more than four of these atoms to any other atom, for this assumption would not explain the apparent non-existence of sulphur tetrahydride, iodine trihydride, and their analogues. It would seem, therefore, that the cause of the decline of hydrogen valency does not reside in the hydrogen atoms, but in the atoms to which they are attached. Indeed, the very regularity of the decline indicates that the former atoms are merely measuring some property of the latter.

(*b*) Assuming that the phenomenon under consideration has its root, not in the hydrogen atoms, but in what may conveniently be called the "central" atom of the hydrides, the matter resolves itself again into two cases. On the one hand, all the valencies of the central atom may be identical with respect to their power of holding hydrogen atoms, some property of the former atom prohibiting the attachment of the full number of the latter; and on the other there may be a difference in the actual nature of the valencies. Taking the first case, all the valency bonds being considered to be alike: The decline of hydrogen valency cannot be connected with the relative affinity of the elements for hydrogen, for the elements of group VII have a higher valency than those of group V, a far greater attraction for hydrogen, and yet only form lower hydrides. Again, within the individual group the stability of the hydride varies enormously, yet the general formula of the typical hydride remains unchanged. Further, the phenomenon cannot be due to the inability of any one atom to hold more than four of any other atoms, as is shown by the existence of such compounds as ammonium chloride and phosphorus pentachloride. Lastly, the fact that the decline in hydrogen valency is as regular as the increase in oxygen valency strongly suggests that the phenomenon is due to the influence of some factor which increases by a constant quantity from group to group, and not to the exercise of some less exactly varying quantity such as chemical affinity. One is therefore led to the conclusion that there may be a difference in the actual nature of the valencies. If this is so, from the very nature of the case the difference should be capable of being detected by hydrogen atoms and hydroxyl groups. It therefore becomes of interest to trace the various ways in which the valencies of the elements may be satisfied by these atoms and groups. All the possible combinations are set forth in the subjoined table.

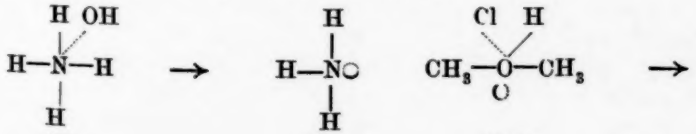
Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
EH	EH_2	EH_3	EH_4	EH_5	EH_6	EH_7	EH_8
E(OH)	EH(OH)	$EH_2(OH)$	$EH_3(OH)$	$EH_4(OH)$	$EH_5(OH)$	$EH_6(OH)$	$EH_7(OH)$
	$E(OH)_2$	$EH(OH)_2$	$EH_2(OH)_2$	$EH_3(OH)_2$	$EH_4(OH)_2$	$EH_5(OH)_2$	$EH_6(OH)_2$
		$E(OH)_3$	$EH(OH)_3$	$EH_2(OH)_3$	$EH_3(OH)_3$	$EH_4(OH)_3$	$EH_5(OH)_3$
			$E(OH)_4$	$EH(OH)_4$	$EH_2(OH)_4$	$EH_3(OH)_4$	$EH_4(OH)_4$
				$E(OH)_5$	$EH(OH)_5$	$EH_2(OH)_5$	$EH_3(OH)_5$
					$E(OH)_6$	$EH(OH)_6$	$EH_2(OH)_6$
						$E(OH)_7$	$EH(OH)_7$
							$E(OH)_8$

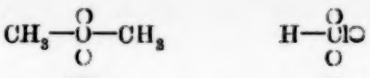
An examination of the table reveals the fact that above the stepped line lies a region of imaginary compounds, whilst below this line is a space containing types of compounds which have a real existence, either in themselves or in their dehydrated forms. It also brings into prominence the remarkable fact that in the first four groups the maximum number of hydrogen atoms which can be attached to the central atom rises regularly to four, and then remains constant throughout the subsequent groups. The four valencies employed in the attachment of these hydrogen atoms can also be satisfied by hydroxyl groups, and may be called "primary" valencies. In group V, however, a fresh type of valency appears, which is not capable of binding hydrogen atoms, but which can hold hydroxyl groups, and may be called "secondary" valency. This secondary valency rises regularly throughout the remaining groups, attaining a maximum of four in the eighth.

It thus appears that the application of a test by means of hydrogen atoms and hydroxyl groups distinguishes between two kinds of valency, primary and secondary, the former of which is capable of holding either hydrogen atoms or hydroxyl groups, the latter having the power of binding hydroxyl groups, but not hydrogen atoms. According to this view, the elements of group V have four primary valencies and one secondary valency, the elements of group VI four primary and two secondary, and so on. This may be represented graphically as below, the ordinary lines representing primary, and the dotted lines secondary valencies.



Chemical considerations made it clear that there is a strong tendency for primary and secondary valencies to unite, thereby lowering the apparent valency of the element by two or multiples of two below the maximum valency. The dehydration of ammonium hydroxide may be represented by I and II, resulting in the production of a valency "loop." On similar lines the dissociation of an oxonium salt is indicated by III and IV; and by analogy, hydrogen chloride may be represented by V:





(IV). (V.)

Hence the formation of ammonium hydroxide from ammonia and water, and of an oxonium salt, depends on the liberation of one primary and one secondary valency by the rupture of a loop, and is a process of addition similar in nature to the addition of hydrogen bromide to ethylene. Thus the addition of a hydrogen atom to the primary valency of a loop involves the addition of a hydroxyl group (or its equivalent) to the secondary valency. The apparent decline in hydrogen valency in groups V—VIII follows as a necessity. This conception of the rupture of a loop giving rise to two kinds of valency bonds, or bonds of different "polarity," is interesting in that it suggests a comparison with the breaking of a conductor through which an electric current is passing.

The matter contained in the foregoing pages leads to the conclusion that each element has a fixed potential valency, such valency being capable of diminution by two or multiples of two through the mutual satisfaction of bonds in pairs. The formation of actual compounds, however, cannot be viewed as a mere mechanical building up of molecules in accordance with the valency requirements of the constituent atoms. Other and important factors, such as electrical character, conditions of symmetry, and available energy, may exercise a modifying influence; and as a result of the complex nature of the forces operative it is only natural that apparent anomalies should be produced. Thus there is the abnormal case of nitric oxide, whilst fluorine is not at present known to form any oxides or oxy-acids. Again, it is easy to conceive of the incomplete neutralisation of valency bonds with the consequent production of the phenomenon of residual affinity, but these side-issues in no way interfere with the conception of valency outlined in the foregoing pages. A single influence at work may produce a set of phenomena according to a fixed law; but where other influences become involved it is not logical to consider that this law should be obeyed with the same degree of rigidity.

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[*Received, August 23rd*, 1916.]

LXXV.—*Overvoltage Tables. Part I. Cathodic Overvoltages.*

By Edgar Newbery.

Electrolytic methods of reduction and oxidation are frequently attended with so much uncertainty as to yield, current efficiency, etc., that in many cases the average chemist prefers to use a purely chemical method even when the electrical method can be made to give a better product with less expense.

This uncertainty is sometimes due to insufficient circulation of the electrolyte, use of unsuitable temperatures, etc., but in the great majority of cases it is largely due to variations in the overvoltage of cathodes or anodes.

Unfortunately, nearly all the data available which deal with the subject of overvoltage relate to that of metals in various solutions under the action of a current too small to be of any practical value to the chemist. The values given by Tafel (*Zeitsch. physikal. Chem.*, 1906, **50**, 712) are direct potential differences and not true overvoltages, and as such are misleading when dealing with electrolytic reductions.

If the potential difference between the experimental electrode and a standard electrode is measured directly while the main current is flowing, the values obtained are always higher than the true overvoltage (that is, the excess of the back electromotive force above that of a hydrogen or oxygen electrode in the same electrolyte). This is due to the electrical resistance of the solution and also of a film of gas which is present on the surface of the electrode. In fact, while the current is flowing, if the resistance of the leads and battery is small compared with that of the cell, the difference of potential between the two electrodes is almost the same as the electromotive force of the battery, the drop of potential between the two electrodes being divided between the films of gas on each electrode and the solution in the ratios of their resistances. Measurements made in this way are therefore quite useless and may be altered at will by merely moving the electrodes further apart or using different shapes and sizes of containing vessels. Hence the results obtained may differ by several thousands per cent. from the true overvoltage (compare T., 1914, **105**, 2422).

The present work was undertaken with the object of supplying data whereby some idea of the best conditions for obtaining suitable overvoltages and keeping these constant where possible may be gained.

Experimental.

The apparatus used was that previously described (T., 1914, **105**, 2420), but the hydrogen electrode was replaced by a mercurous sulphate electrode when working with sulphuric acid solutions and by a mercuric oxide electrode when working with sodium hydroxide solutions.

These standard electrodes were tested by comparison with hydrogen electrodes in normal sulphuric acid and sodium hydroxide respectively, and found to agree well with the generally accepted values. The mercurous sulphate electrode was taken as 0·70 volt positive to the hydrogen electrode in normal sulphuric acid, and the mercuric oxide electrode as 0·93 volt positive to the hydrogen electrode in normal sodium hydroxide. The same standard electrodes were used in measuring anodic overvoltages, but in this case there is still some uncertainty as to the true value of the normal potential of the oxygen electrode. The figures given have been calculated on the assumption that the potential of the oxyhydrogen cell is 1·13 volts. Hence the mercurous sulphate electrode is considered as 0·43 volt negative to the oxygen electrode in normal sulphuric acid and the mercuric oxide electrode as 0·20 volt negative to the oxygen electrode in normal sodium hydroxide solution. Further investigation of the oxyhydrogen cell may show that the anodic overvoltages calculated on this assumption may all require to be reduced by 0·10 volt (see *Zeitsch. physikal. Chem.*, 1906, **55**, 473).

No special care was taken in most cases to secure great purity of the metals used, as it was considered that the figures obtained would be of more value if they related to commercial samples readily procurable. Individual cases where slight impurities exert considerable influence on the overvoltage of a metal are referred to later.

In order to secure, as far as possible, a uniformity in the surfaces exposed to the electrolyte, the electrodes before use were rubbed with Oakey's No. 1 glass-paper. In the time experiments this was done at the beginning of each series of readings.

In the experiments on the effect of current density, the electrode was in all cases (except those specially noted) allowed two minutes with a current density of 2 milliamperes per sq. cm. for the overvoltage to settle down to a fairly constant value before taking any readings. The current density was then increased as shown in the tables, one minute being allowed before each reading, until the maximum was reached, and then decreased in the same way. The first set of readings thus obtained is given under column *A*

in the tables, and the average of at least four subsequent sets, obtained as described, under column *B*. Column *B* therefore shows the combined effect of time and exposure to the action of a high current density.

In most cases these two effects are similar, the action of the high current density being merely to hasten the effect which would otherwise be produced by time alone. Certain cases, however, occur in which this is not so, and these are referred to in the notes on individual electrodes.

All the measurements were taken at ordinary temperature (15° approx.).

Current densities (C.D.) are given in milliamperes per sq. cm. (=amperes per sq. dm. × 10).

The following electrodes were in the form of thin sheets: gold, platinum, copper, silver, nickel, cobalt, aluminium, and tungsten, all of 1 sq. cm. total exposed surface. The rest were in the form of small rods.

Cathodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Au.	*B.* Au.	*A.* Pt.	*B.* Pt.	*A.* Cu.	*B.* Cu.	*A.* Ag.	*B.* Ag.
2	0·31	0·38	0·05	0·20	0·37	0·34	0·27	0·33
4	0·32	0·39	0·06	0·19	0·38	0·35	0·28	0·33
6	0·32	0·38	0·06	0·18	0·38	0·35	0·28	0·33
10	0·32	0·38	0·06	0·16	0·39	0·36	0·27	0·32
20	0·31	0·36	0·06	0·15	0·40	0·35	0·25	0·31
50	0·31	0·36	0·07	0·13	0·39	0·34	0·24	0·30
100	0·30	0·36	0·07	0·12	0·38	0·33	0·23	0·29
200	0·29	0·36	0·08	0·11	0·37	0·33	0·23	0·28
400	0·28	0·34	0·09	0·07	0·35	0·32	0·23	0·25
1000	0·26	0·30	0·08	−0·01	0·32	0·30	0·22	0·16
2000	0·24	0·24	0·01	−0·02	0·30	0·28	0·11	0·10

Cathodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Pb.	*B.* Pb.	*A.* Zn.	*B.* Zn.	*A.* Ni.	*B.* Ni.	*A.* Co.	*B.* Co.
2	0·74	0·45	0·68	0·70	0·16	0·29	0·27	0·23
4	0·75	0·46	0·69	0·70	0·17	0·30	0·27	0·24
6	0·73	0·46	0·69	0·71	0·17	0·31	0·28	0·24
10	0·71	0·47	0·69	0·71	0·18	0·30	0·28	0·24
20	0·67	0·46	0·70	0·72	0·18	0·29	0·27	0·25
50	0·64	0·44	0·71	0·74	0·18	0·26	0·27	0·25
100	0·59	0·42	0·71	0·75	0·19	0·24	0·26	0·26
200	0·58	0·39	0·71	0·75	0·19	0·21	0·26	0·26
400	0·54	0·35	0·72	0·75	0·18	0·18	0·25	0·25
1000	0·53	0·30	0·72	0·76	0·17	0·11	0·25	0·24
2000	0·50	0·28	0·72	0·75	0·15	0·06	0·23	0·20

Cathodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Sn.	*B.* Sn.	*A.* Al.	*B.* Al.	*A.* Hg.	*B.* Hg.	*A.* W.	*B.* W.
2	0·62	0·44	0·44	0·18	0·21	0·61	0·32	0·28
4	0·66	0·45	0·48	0·14	0·21	0·63	0·32	0·28
6	0·67	0·46	0·49	0·13	0·21	0·65	0·32	0·29
10	0·66	0·47	0·50	0·11	0·21	0·66	0·32	0·29
20	0·66	0·48	0·49	0·12	0·21	0·66	0·32	0·28
50	0·65	0·49	0·49	0·15	0·21	0·66	0·31	0·28
100	0·63	0·49	0·48	0·19	0·36	0·53	0·31	0·27
200	0·60	0·48	0·47	0·22	0·38	0·46	0·31	0·26
400	0·54	0·41	0·40	0·20	0·30	0·37	0·30	0·26
1000	0·34	0·33	0·16	0·14	0·22	0·29	0·26	0·22
2000	0·30	0·29	0·11	0·08	0·19	0·26	0·20	0·19

Cathodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Sb.	*B.* Sb.	*A.* Bi.	*B.* Bi.	*A.* C1.	*B.* C1.	*A.* C2.	*B.* C2.
2	0·44	0·38	0·49	0·41	0·38	0·33	0·44	0·32
4	0·45	0·41	0·51	0·42	0·42	0·37	0·44	0·34
6	0·45	0·42	0·52	0·43	0·45	0·44	0·44	0·36
10	0·45	0·42	0·53	0·44	0·48	0·49	0·43	0·35
20	0·44	0·42	0·54	0·44	0·54	0·56	0·42	0·35
50	0·44	0·42	0·53	0·43	0·60	0·62	0·40	0·35
100	0·43	0·43	0·52	0·42	0·67	0·67	0·39	0·35
200	0·42	0·42	0·51	0·37	0·71	0·71	0·38	0·37
400	0·41	0·41	0·49	0·32	0·75	0·76	0·38	0·40
1000	0·40	0·40	0·36	0·19	0·77	0·80	0·38	0·39
2000	0·38	0·37	0·12	0·08	0·76	0·78	0·38	0·39

C1 Gas carbon.
C2 Artificial graphite.

Cathodic Overvoltage in N-*Sulphuric Acid.*

Iron alloys.

Current density.	*A.* Fe1.	*B.* Fe1.	*A.* Fe2.	*B.* Fe2.	*A.* Fe3.	*B.* Fe3.	*A.* Fe4.	*B.* Fe4.
2	0·27	0·24	0·26	0·20	0·26	0·26	0·16	0·15
4	0·27	0·25	0·27	0·21	0·27	0·26	0·17	0·15
6	0·27	0·26	0·28	0·22	0·27	0·26	0·17	0·16
10	0·27	0·26	0·28	0·22	0·28	0·26	0·19	0·16
20	0·28	0·27	0·28	0·22	0·28	0·26	0·22	0·17
50	0·29	0·27	0·28	0·23	0·28	0·27	0·26	0·19
100	0·30	0·27	0·27	0·23	0·29	0·27	0·28	0·21
200	0·30	0·27	0·27	0·22	0·29	0·27	0·30	0·22
400	0·31	0·28	0·27	0·22	0·30	0·27	0·31	0·23
1000	0·29	0·27	0·25	0·21	0·30	0·28	0·32	0·26
2000	0·27	0·26	0·23	0·21	0·29	0·27	0·32	0·26

Fe1 pure iron, forged bar.
Fe2 carbon steel, 0·5 % carbon.
Fe3 chromium steel, 10 % chromium.
Fe4 "tantiron," a non-corrodible cast iron.

Cathodic Overvoltage in N-*Sulphuric Acid.*

Plated and amalgamated surfaces.

Current density.	*A.* CuAg.	*B.* CuAg.	*A.* NiAg.	*B.* NiAg.	*A.* ZnHg.	*B.* ZnHg.	*A.* PbHg.	*B.* PbHg.
2	0·26	0·12	0·16	0·17	0·85	0·87	0·79	0·86
4	0·28	0·13	0·18	0·18	0·87	0·87	0·80	0·86
6	0·28	0·15	0·18	0·18	0·88	0·87	0·80	0·86
10	0·29	0·16	0·18	0·19	0·88	0·87	0·81	0·86
20	0·29	0·17	0·19	0·20	0·89	0·88	0·82	0·86
50	0·28	0·19	0·19	0·21	0·89	0·88	0·84	0·85
100	0·26	0·19	0·20	0·22	0·89	0·87	0·84	0·85
200	0·25	0·20	0·18	0·22	0·88	0·86	0·84	0·84
400	0·23	0·19	0·18	0·19	0·88	0·85	0·83	0·83
1000	0·21	0·19	0·13	0·14	0·86	0·84	0·82	0·82
2000	0·18	0·18	0·09	0·10	0·84	0·84	0·81	0·81

CuAg electrode prepared by adding 0·01 gram of silver sulphate to electrolyte.

NiAg electrode prepared by immersing nickel for ½ a minute in silver potassium cyanide plating solution.

Cathodic Overvoltage in N-*Sulphuric Acid.*

Time Experiments.—For these experiments the same cathodes were used as in the previous series, the surfaces being renewed in each case by thorough rubbing with No. 1 glass-paper. The results, with one exception, are identical with those which would have been obtained by the use of an entirely new set of electrodes. The one exception is in the case of graphite. Some new graphite electrodes contain so much adsorbed oxygen capable of uniting with the active hydrogen present that a time experiment with low current density gives a series of negative values for the overvoltage during the first fifteen minutes, and this does not at all represent the true overvoltage of the electrode. This property of new gas carbon or graphite electrodes should be borne in mind when carrying out electrolytic reductions, otherwise incorrect estimates of the current efficiency may be made.

The cleaning with glass-paper was repeated with each electrode before commencing each series of thirty minutes' readings. In the case of mercury, fresh samples were taken from the stock bottle for each series.

Platinum.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·01	0·02	0·02	0·02	0·02	0·03	0·03	0·03	0·03	0·04
10	0·02	0·03	0·03	0·04	0·04	0·05	0·05	0·06	0·06	0·07
100	0·02	0·03	0·03	0·03	0·04	0·06	0·07	0·08	0·08	0·09
1000	0·02	0·03	0·03	0·04	0·04	0·05	0·04	0·04	0·03	0·02

Copper.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·31	0·32	0·32	0·31	0·30	0·30	0·30	0·29	0·29	0·29
10	0·29	0·29	0·29	0·29	0·29	0·28	0·28	0·27	0·27	0·27
100	0·28	0·28	0·28	0·27	0·27	0·27	0·27	0·27	0·26	0·26
1000	0·17	0·16	0·15	0·15	0·15	0·14	0·13	0·13	0·13	0·14

Silver.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·28	0·29	0·29	0·29	0·29	0·31	0·31	0·31	0·32	0·32
10	0·29	0·29	0·29	0·30	0·30	0·31	0·31	0·32	0·32	0·33
100	0·27	0·26	0·25	0·24	0·23	0·22	0·23	0·23	0·23	0·22
1000	0·15	0·14	0·14	0·15	0·15	0·17	0·16	0·17	0·17	0·16

Lead.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·72	0·78	0·80	0·82	0·84	0·76	0·75	0·74	0·72	0·71
10	0·72	0·73	0·72	0·71	0·70	0·69	0·69	0·69	0·69	0·68
100	0·64	0·64	0·64	0·62	0·61	0·58	0·56	0·55	0·55	0·52
1000	0·38	0·36	0·35	0·35	0·35	0·34	0·34	0·35	0·36	0·36
First series repeated after the last, without cleaning electrode.										
1	0·36	0·45	0·49	0·52	0·52	0·55	0·54	0·52	0·52	0·54

Tin.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·25	0·54	0·56	0·59	0·60	0·60	0·61	0·61	0·61	0·61
10	0·50	0·57	0·59	0·59	0·60	0·60	0·60	0·60	0·61	0·62
100	0·55	0·57	0·55	0·54	0·51	0·45	0·41	0·39	0·40	0·39
1000	0·35	0·33	0·32	0·31	0·31	0·30	0·30	0·30	0·31	0 31

Mercury.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·51	0·64	0·60	0·58	0·58	0·59	0·55	0·56	0·54	0·56
10	0·39	0·30	0·30	0·29	0·32	0·40	0·45	0·49	0·49	0·50
100	0·45	0·48	0·54	0·48	0·49	0·52	0·48	0·46	0·44	0·45*
1000	−0·02	0·00	0·04	0·01	0·04	0·06	0·12	0·12	0·17	0·19

* Fell to 0·08 after further 30 minutes.

Graphite.

Current density.	Time in Minutes. 1	2	3	4	5	10	15	20	25	30
1	−0·01	+0·02	0·05	0·07	0·10	0·15	0·18	0·20	0·22	0·23
10	0·42	0·48	0·49	0·48	0·49	0·48	0·47	0·47	0·46	0·46
100	0·44	0·45	0·44	0·44	0·44	0·43	0·43	0·42	0·42	0·43
1000	0·41	0·45	0·47	0·49	0·50	0·60	0·61	0·62	0·62	0·61

Amalgamated Zinc.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·82	0·83	0·84	0·85	0·86	0·86	0·87	0·88	0·88	0·88
10	0·88	0·88	0·88	0·88	0·88	0·88	0·88	0·88	0·88	0·88
100	0·88	0·88	0·88	0·88	0·87	0·87	0·86	0·86	0·86	0·86
1000	0·82	0·82	0·83	0·83	0·83	0·84	0·84	0·84	0·84	0·84
	First series repeated 3 days later with same electrode.									
1	0·78	0·80	0·80	0·80	0·80	0·82	0·83	0·84	0·83	0·83

Cathodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Au.	*B.* Au.	*A.* Pt.	*B.* Pt.	*A.* Cu.	*B.* Cu.	*A.* Ag.	*B.* Ag.
2	0·44	0·38	0·16	0·21	0·50	0·43	0·43	0·35
4	0·46	0·39	0·17	0·22	0·52	0·46	0·44	0·37
6	0·46	0·40	0·19	0·24	0·53	0·47	0·45	0·38
10	0·47	0·40	0·20	0·25	0·53	0·49	0·45	0·39
20	0·48	0·41	0·21	0·26	0·52	0·50	0·45	0·39
50	0·48	0·41	0·22	0·28	0·51	0·50	0·44	0·39
100	0·48	0·42	0·22	0·28	0·51	0·51	0·43	0·40
200	0·48	0·42	0·22	0·28	0·50	0·51	0·43	0·40
400	0·47	0·41	0·21	0·28	0·49	0·51	0·42	0·40
1000	0·47	0·41	0·20	0·27	0·49	0·50	0·41	0·39
1200	0·45	0·40	0·19	0·27	0·48	0·50	0·40	0·38

Cathodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Pb.	*B.* Pb.	*A.* Zn.	*B.* Zn.	*A.* Ni.	*B.* Ni.	*A.* Co.	*B.* Co.
2	0·57	0·58	0·59	0·56	0·18	0·23	0·25	0·48
4	0·57	0·64	0·60	0·58	0·20	0·23	0·27	0·53
6	0·57	0·65	0·60	0·69	0·20	0·24	0·28	0·56
10	0·57	0·67	0·60	0·59	0·20	0·24	0·28	0·61
20	0·57	0·68	0·60	0·60	0·20	0·24	0·29	0·67
50	0·60	0·69	0·59	0·60	0·21	0·24	0·29	0·69
100	0·61	0·69	0·59	0·60	0·21	0·24	0·29	0·69
200	0·63	0·69	0·58	0·60	0·21	0·25	0·30	0·69
400	0·64	0·68	0·57	0·59	0·22	0·24	0·30	0·68
1000	0·64	0·67	0·56	0·58	0·21	0·24	0·29	0·65
1200	0·65	0·67	0·56	0·57	0·21	0·23	0·29	0·64

Cathodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Sn.	*B.* Sn.	*A.* Al.	*B.* Al.	*A.* Hg	*B.* Hg.	*A.* W.	*B.* W.
2	0·57	0·57	0·52	0·48	0·92	0·67	0·31	0·27
4	0·57	0·60	0·52	0·49	0·96	0·67	0·31	0·27
6	0·57	0·62	0·52	0·49	0·97	0·68	0·31	0·27
10	0·57	0·63	0·52	0·49	0·98	0·69	0·31	0·27
20	0·57	0·64	0·52	0·49	0·99	0·69	0·30	0·28
50	0·58	0·65	0·52	0·50	1·02	0·69	0·29	0·28
100	0·59	0·65	0·52	0·50	1·05	0·70	0·28	0·28
200	0·59	0·63	0·51	0·50	1·02	0·71	0·28	0·29
400	0·60	0·63	0·51	0·50	1·01	0·79	0·28	0·29
1000	0·61	0·63	0·51	0·49	0·99	0·88	0·28	0·29
1200	0·61	0·62	0·51	0·49	0·95	0·95	0·28	0·28

Cathodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Sb.	*B.* Sb.	*A.* Bi.	*B.* Bi.	*A.* C1.	*B.* C1.	*A.* C2.	*B.* C2.
2	0·59	0·62	0·59	0·59	−0·17	0·37	−0·31	0·42
4	0·63	0·64	0·66	0·65	−0·15	0·41	−0·28	0·47
6	0·64	0·65	0·70	0·68	−0·12	0·46	−0·24	0·49
10	0·65	0·66	0·73	0·71	−0·02	0·53	−0·17	0·54
20	0·65	0·67	0·75	0·74	+0·19	0·62	−0·04	0·56
50	0·65	0·67	0·77	0·75	0·42	0·66	+0·64	0·60
100	0·65	0·67	0·77	0·76	0·65	0·70	0·67	0·64
200	0·64	0·66	0·77	0·76	0·74	0·72	0·69	0·67
400	0·63	0·65	0·77	0·76	0·79	0·73	0·70	0·69
1000	0·61	0·63	0·77	0·74	0·78	0·77	0·71	0·71
1200	0·60	0·61	0·76	0·73	0·77	0·77	0·71	0·71

C1 gas carbon.
C2 graphite.

Cathodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Fe1.	*B.* Fe1.	*A.* Fe4.	*B.* Fe4.	*A.* ZnHg.	*B.* ZnHg.	*A.* PbHg.	*B.* PbHg.
2	0·27	0·28	0·18	0·16	0·91	0·63	0·92	0·65
4	0·30	0·31	0·23	0·20	0·96	0·65	0·97	0·67
6	0·31	0·32	0·27	0·22	0·97	0·66	0·99	0·68
10	0·32	0·33	0·31	0·25	0·98	0·67	1·01	0·69
20	0·33	0·34	0·35	0·30	1·02	0·68	1·04	0·69
50	0·34	0·34	0·37	0·35	1·07	0·68	1·07	0·70
100	0·34	0·35	0·38	0·37	1·08	0·68	1·12	0·72
200	0·34	0·35	0·39	0·38	1·06	0·69	1·12	0·74
400	0·34	0·35	0·39	0·39	1·03	0·72	1·12	0·81
1000	0·33	0·34	0·40	0·39	1·01	0·93	1·23	0·96
1200	0·33	0·34	0·39	0·39	0·98	1·00	1·18	1·04

Fe1 pure iron.
Fe4 tantiron.

Lead in N-NaOH.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·48	0·47	0·47	0·46	0·46	0·44	0·44	0·43	0·43	0·42
10	0·49	0·50	0·50	0·51	0·51	0·51	0·51	0·51	0·51	0·51
100	0·53	0·55	0·58	0·61	0·63	0·67	0·70	0·72	0·73	0·73
1000	0·65	0·69	0·70	0·70	0·71	0·72	0·71	0·71	0·71	0·71

Nickel.

Current density.	Time in minutes.									
	1	2	3	4	5	10	15	20	25	30
1	0·15	0·15	0·15	0·15	0·15	0·16	0·16	0·16	0·16	0·16
10	0·16	0·16	0·16	0·16	0·16	0·16	0·16	0·17	0·17	0·17
100	0·17	0·17	0·17	0·17	0·17	0·17	0·17	0·17	0·17	0·17
1000	0·19	0·19	0·19	0·19	0·19	0·19	0·19	0·20	0·20	0·20

Amalgamated Lead.

Current density.	Time in minutes.									
	1	2	3	4	5	10	15	20	25	30
1	0·89	0·89	0·88	0·87	0·86	0·85	0·79	0·76	0·74	0·73
10	1·09	1·08	1·05	1·00	0·96	0·87	0·79	0·76	0·74	0·72
100	1·10	1·06	1·00	0·95	0·91	0·76	0·72	0·70	0·71	0·72
1000	1·16	1·11	1·08	1·06	1·03	0·95	0·88	0·85	0·81	0·76

Cathodic Overvoltage. Remarks on Individual Electrodes.

Gold.—The back electromotive force is erratic,* especially in acid electrolyte. The overvoltage rises rapidly at first, but falls to much lower values after repeated subjection to high current densities. In alkaline electrolyte the initial rise is very slight, but the average values are higher than in acid and less affected by high current densities.

Platinum.—The overvoltage in acid is very low and steady, but unless the surface is platinised the time effect is very great, especially at low current densities. In twenty-four hours, with a current density of 300 milliamperes per sq. cm., the overvoltage exceeds 0·5 volt. After continued use with high current densities the surface is automatically platinised, and it is then difficult to raise the overvoltage above a very low value.

In alkaline electrolyte the overvoltage is considerably higher, but the time and current density effects are similar to those in acid.

Copper.—The overvoltage is fairly steady and low, but especially susceptible to traces of impurity in electrode or electrolyte, such impurities usually tending to lower the overvoltage. Hence pure electrolytic copper generally has a higher overvoltage than the ordinary commercial metal, although with other metals electrodeposited surfaces, as a rule, give lower values.

* The terms "erratic" and "steady" as applied to overvoltage are intended to refer only to the sudden, jerky changes observed when taking single measurements. They are not meant to apply to the gradual rising and falling observed when a series of measurements is made, for which the terms "variable" and "constant" are employed.

On comparing the two tables showing the effect of current density and time respectively in acid electrolyte, it will be seen that the values at high current density are quite different. This is due to the fact that the overvoltage of copper (and some other metals, especially mercury) depends greatly on the previous history of the metal. In the time experiments the high current density was applied at once, and not gradually approached as in the current density series. It is evident from these figures that if copper is to be used as cathode in any work where variation of overvoltage may lead to variation of the products (for example, the reduction of nitrates) the greatest care must be taken in the preparation of the electrode to ensure concordant results.

The overvoltage in alkaline electrolyte is decidedly higher than in acid, and also tends to increase with time at the higher current densities, probably owing to the formation of a sodium–copper alloy.

Silver.—The overvoltage is more constant than that of copper and less susceptible to slight impurities. There is a tendency to rise in acid electrolyte and also in alkali at low current density. When electro-deposited in a spongy condition from a solution of the sulphate the overvoltage is very low, but an electrode prepared in this way is unsuitable for most reductions requiring low overvoltage on account of the tendency of the deposit to break away from the electrode surface. Cathodes of copper or nickel with a fairly thick coating of rough silver deposited in a cyanide bath are useful where moderated reductions are required.

Lead.—This is probably more used in electrolytic work than any other metal, and is capable of acquiring a very high overvoltage, but this high overvoltage is easily destroyed if considerable care is not exercised. The most frequent causes leading to reduction of the overvoltage of lead are impurities in the metal and subjection to too high a current density. The slightest trace of some metals, especially platinum, is sufficient to render a lead cathode useless for powerful reductions. The application of a high current density is sufficient permanently to lower the overvoltage to 0·55 volt in acid electrolyte, but in alkali the overvoltage is raised by similar treatment.

The highest values (up to 0·8 volt) are obtained in acid electrolyte by reduction of an electrolytically oxidised surface. Since this high value falls somewhat rapidly even with moderate current densities, a considerable improvement in the yield from some substances reducible with difficulty may often be produced by reversing the current through the electrolytic cell for a short period from time to time during the experiment.

The sample of lead used for this work was pure electrolytic metal obtained by Betts's process.

Violent stirring of the electrolyte near a lead electrode may lower the overvoltage by as much as 0·2 volt in acid electrolyte. A small spiral glass stirrer about 0·3 cm. wide was spun by an electromotor with a speed of about 3000 revolutions per minute at a distance of 1 cm. from the experimental cathode. With a current density of 10 milliamperes per sq. cm. the overvoltage fell from 0·55 volt to 0·35 volt while the stirring was proceeding. The magnitude of the fall in overvoltage is approximately proportional to the violence of the stirring.

Zinc.—This metal has as great or greater overvoltage than lead, and also has the advantage that the high overvoltage is not destroyed, but rather increased by subjection to the action of a high current density. The effect of time is also to increase the overvoltage both in acid and in alkali, so that in many respects it is decidedly preferable to lead as a cathode for powerful reductions, especially when a fairly strong current is required. Against these advantages it has the disadvantages of brittleness and lack of the pliability which is frequently found useful in the case of lead, and also it is liable to attack by the electrolyte when no current is flowing. The back electromotive force is much steadier than that of lead and is less affected by stirring the electrolyte.

Nickel.—This metal forms a very useful substitute for platinum in many cases where a low overvoltage is required, but it is, unfortunately, very difficult to keep the overvoltage down. Roughening the surface mechanically or depositing a thin coating of rough silver on the metal depresses the overvoltage for a time.

With a current density of 10 milliamperes per sq. cm. the overvoltage in acid rose from 0·18 to 0·38 volt in ten minutes, and then fell to 0·33 volt after a further twenty minutes. Interrupting the current for a few seconds causes a temporary fall in the overvoltage, but it rapidly rises to a still higher value on renewing the current.

In alkali the overvoltage is much more constant, the time effect being almost nil at all current densities, although a small rise is produced by subjecting the metal to the action of a very high current density.

Cobalt.—In acid electrolyte the overvoltage is of the same order as that of nickel, but is much more constant and less liable to change either with time or current density.

In alkali the behaviour is remarkable. At first the overvoltage is little higher than that of nickel, but gradually rises with time. At very high current densities sudden rapid rises of overvoltage

take place, sometimes directly the current density reaches a high value and at others after repeatedly raising and lowering the current density between the limits 2 and 2000 milliamperes per sq. cm. This rise may be as much as 0·4 volt, and after it has taken place the high overvoltage persists at all current densities, the metal then behaving like a new electrode, such as lead or zinc. Cleaning with glass-paper at once restores the normal overvoltage; hence the effect is purely a surface one and is probably due to the formation of a cobalt–sodium alloy. Series *B* in the table gives the values after the change has taken place.

Tin.—The overvoltage of tin is somewhat lower than, but similar to, that of lead. Just as in the case of lead, it is permanently lowered in acid electrolyte by the action of high current densities, although it is necessary to apply a higher current density than with lead. The rise of overvoltage with time at low current densities is much slower than in the case of lead, and the subsequent fall, if it takes place at all, is very slight.

The overvoltage of tin in alkali is almost identical with that of lead.

Aluminium.—This metal when first used has a fairly high overvoltage in acid electrolyte, but when subjected to a high current density the overvoltage suddenly falls by about 0·25 volt. This lowered value persists at other current densities, although there appears to be a tendency slowly to revert to the higher values with current densities below 10 milliamperes per sq. cm.; hence the overvoltage reaches a minimum at this current density. It appears impossible to apply a current density of 500 milliamperes per sq. cm. without this change taking place after a few seconds; also the change occurs more quickly with the polished metal than with a rough surface.

Mercury and Amalgamated Surfaces.—Pure mercury has the most variable overvoltage of all the electrodes tried, and varies by sudden jumps from high to low and vice versâ in the most unaccountable manner. During the first series of measurements given in the table it behaved like a low overvoltage metal, and the potential was fairly steady. In all other cases the potential was very erratic, and considerable difficulty was frequently encountered to obtain even an approximate measurement of the overvoltage. The results in acid electrolyte shown in column *B* are the mean of eight series of readings, and although the highest value given here is 0·66 volt and the lowest 0·19 volt, yet values up to 0·78 volt at low current density and down to −0·05 volt at high current density are frequently obtained. Sometimes after

current has been passing at fairly high density for long periods the overvoltage will suddenly drop by as much as 0·5 volt, and continue in this condition when the current density is changed between wide limits, and even after breaking the circuit for half an hour. After using mercury as cathode for long periods of time and then breaking the circuit, bubbles of gas may be observed rising to the surface of the metal, rapidly at first, but some gas may still be seen rising an hour after stopping the current.

In alkali the overvoltage attains very high values for a short time only, but in this case it is known that sodium amalgam is formed, so that we are no longer dealing with the pure metal.

Amalgamation raises the overvoltage of all metals. In the case of copper the elevation of the overvoltage is great, but only lasts for a few hours, and the erratic behaviour of a mercury electrode is still evident. In the cases of zinc and lead the behaviour is quite different. In acid electrolyte the overvoltage of both electrodes is higher, steadier, and less affected by changes of current density and time than that of any of the pure metals which they contain. The erratic behaviour of a mercury electrode is conspicuous by its entire absence in amalgamated zinc or lead electrodes, and hence these would appear to be ideal electrodes for the most powerful reductions. Unfortunately, this is not always the case, as the surface of the electrode sometimes becomes broken up and covered with a grey film of "dusty" mercury which lowers the overvoltage considerably. This is especially liable to occur in the presence of organic reducible substances. Nevertheless, an amalgamated zinc electrode will occasionally induce reductions where all other electrodes fail, and its high overvoltage is easily restored by merely rubbing the surface with the finger or washing in dilute acid.

Freshly prepared surfaces have the highest overvoltage, and there is always a slight fall of overvoltage as the mercury sinks into the metal surface. With amalgamated zinc the fall in three days was 0·04 volt, whilst with amalgamated copper the maximum overvoltage fell from 0·7 volt to 0·35 volt in eighteen hours.

In alkali electrolyte the formation of sodium amalgam lowers the overvoltage considerably, and there is little to choose between the three electrodes mercury, lead amalgam, zinc amalgam. Mercury alone is perhaps to be avoided, owing to the waste of current which occurs during the formation of sodium amalgam. In concentrated sodium hydroxide solution the mercury electrode solidifies before much reduction can be induced in a difficultly reducible substance. Very beautiful fern-like growths of crystal-

line sodium amalgam are sometimes observed shooting up from the mercury surface and clinging to the sides of the electrolytic cell.

Tungsten.—The overvoltage of tungsten is remarkable for its steadiness, its very small variation with time and current density, and the speed with which it attains its maximum. Whilst platinum at low current density requires days to attain its maximum overvoltage, tungsten requires only a few seconds. Except at the highest current densities, the overvoltage is almost the same in acid and alkali.

Antimony and Bismuth.—These two metals have very similar overvoltages, those in alkaline electrolyte being about 0·2 volt higher in both cases. The back electromotive force of bismuth in acid electrolyte is very erratic, whilst in alkaline electrolyte it is steady. That of antimony is steady in both cases.

When used as cathode in alkali, bismuth acquires a dark bronze colour and the overvoltage falls slightly. The overvoltage of antimony tends to rise under similar conditions and its colour is unchanged, but in both cases the time effect is very small.

Carbon.—The electrodes used were small rods of electric light carbon and artificial graphite, both made by Le Carbone Cie, Paris.

Fresh rods were used in acid and alkali, but owing to the time necessary to saturate such porous electrodes with gas a current of 5 milliamperes was allowed to pass for ten minutes in each case before taking readings. As will be seen from the tables, this was sufficient in acid electrolyte to avoid a series of negative values, but not in alkali.

A notable feature of both electrodes is the very high current density required to produce the maximum overvoltage, and also the fact that in acid electrolyte the overvoltage rises to its highest values after long use at very high current density—a feature not observed with any other electrode.

At low current densities the overvoltages of gas, carbon, and graphite are nearly the same, but at higher current densities that of the former is decidedly greater, especially in acid electrolyte.

*Iron and Iron Alloys.**—A number of iron alloys have been examined in order to find if any connexion exists between overvoltage and corrodibility.

Of those given in the tables, carbon steel is the most liable to corrosion. Pure iron shows considerable resistance to corrosion,

* The author is indebted to Sir Robert Hadfield, F.R.S., for the samples of pure iron, carbon steel, and chrome steel, and to Messrs. Lennox & Co. for the sample of "tantiron."

high chrome steel (so-called stainless steel) still greater, and "tantiron" appears to be almost rustless.

Corresponding with these facts, it may be noted that the maximum overvoltage of carbon steel in acid electrolyte is obtained with a current density of 50 milliamperes per sq. cm., that of pure iron with 400, that of chrome steel with 1000, and that of "tantiron" with more than 2000 milliamperes per sq. cm.

A small strip of common, rusty sheet-iron cleaned and used in the same way gave its maximum overvoltage with a current density of only 4 milliamperes per sq. cm.

It appears, therefore, that an iron alloy which requires a high current density to produce its maximum overvoltage is likely to offer resistance to corrosion.

All the iron alloys have quite low overvoltages in acid and alkaline electrolytes, and, with the exception of "tantiron," are but slightly affected by time and current density changes.

Probably perforated sheets of "tantiron" or gauze of chrome-steel wire could with advantage be used in large-scale work as cathodes for high-efficiency reductions in acid electrolytes.

Silvered Copper and Nickel.—Just as mercury on the surface of a metal can raise the overvoltage of the electrode above that of either the metal itself or mercury, so silver deposited on the surface of another metal lowers the overvoltage below that of either the metal itself or of silver.

The same disadvantage exists here as in the case of amalgamated surfaces, in that the surface coating tends to become broken up in some electrolytes and the overvoltage rises to that of the underlying metal. Hence, whilst these electrodes are useful as a substitute for platinum where a moderated reducing action is required for a short time, they are generally unsuitable for long-continued electrolyses in many electrolytes.

Notes on the Use of the Tables.

Whilst it is of fundamental importance that the overvoltage of an electrode should be taken into account when studying electrolytic reductions and oxidations, it must not be forgotten that in many cases the metal itself exerts a specific effect on the required reaction which may be of equal or greater importance than that of the overvoltage. This is especially the case with electrodes of nickel, copper, or platinum, which sometimes effect reductions with greater ease than those of lead or zinc, although the cathodic overvoltages of the latter are much greater than those of the former.

If no such specific action is exerted, then the electrode with the highest overvoltage may be depended on to give the best current efficiency when very powerful reductions are required, and conditions should generally be arranged by reference to the tables such as will secure the highest possible overvoltages.

If the required reduction proceeds easily with a cathode of low overvoltage, nothing is to be gained by using one of high overvoltage, but rather a useless waste of energy occurs, and the solutions tend to be overheated.

When once the most suitable electrode has been chosen the tables may be referred to for guidance in determining the conditions under which the overvoltage is most suitable and most constant. Unless the action proceeds with great ease and high current efficiency variation of the overvoltage is certain to result in variation of the yield and current efficiency.

ELECTRO-CHEMICAL LABORATORIES,
MANCHESTER UNIVERSITY. [*Received, May 23rd,* 1916.]

LXXVI.—*Overvoltage Tables. Part II. Anodic Overvoltages.*

By EDGAR NEWBERY.

THE determinations of anodic overvoltages were carried out in the same way as those of cathodic overvoltages described in Part I. The scope of the experiments is, however, limited to those electrodes which either resist the oxidising action of the anion (for example, platinum, gold, etc.) or become passive under anodic treatment (for example, iron, nickel, etc.). Electrodes, such as zinc, copper, etc., which dissolve readily under the influence of the sulphation give a series of negative values for the anodic overvoltages in dilute sulphuric acid at all current densities. Some electrodes become covered with an electrically conducting peroxide, and these, of which lead is a notable example, frequently give very high anodic overvoltages. Others (the valve metals) become coated with badly conducting oxides or peroxides, and many new phenomena occur. Thus tungsten in nitric acid, when made the anode in a cell with an applied potential of 10 volts, allowed less than 10^{-4} ampere per sq. cm. to pass, although the surface appeared quite bright and unaltered. If an invisible film of tungsten oxide can give a resistance of 10^5 ohms per sq. cm., the specific resistance of such a substance must be enormous. Very few electrodes are capable of withstanding anodic treatment for any length of time without disintegration. Platinum is, of course, the best in acid electrolytes,

but in dilute sulphuric acid a lead plate coated with lead peroxide is only attacked to a very slight extent if the liquid is not stirred. Compressed blocks of manganese dioxide (agglomerate blocks) also form useful anodes in dilute sulphuric acid. In certain cases the disintegrating action of the anions appears to be alone responsible for the destruction of the electrode. A gold electrode suffers badly in this way, being torn to pieces after a few hours' use in moderately concentrated sulphuric acid. A lead or iron plate in the same acid becomes covered with an insulating coating of lead or iron sulphate. If the acid is much above 80 per cent. in strength, therefore, these metals cannot be used as anodes.

In alkali, the anodic disintegration appears much less as a rule, specially in concentrated solutions.

Pure hard nickel appears to be most resistant, graphite is good if the current density is kept low, but silver is readily attacked.

Other cases of anodic disintegration will be referred to under the notes on individual electrodes.

Anodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Au.	*B.* Au.	*A.* Pt.	*B.* Pt.*	*A.* Ag.	*B.* Ag.
2	0·86	0·87	0·81	0·85	—	—
4	0·87	0·87	0·83	0·85	—	—
6	0·86	0·88	0·84	0·86	—	—
10	0·85	0·87	0·85	0·86	—	—
20	0·84	0·86	0·85	0·86	—	—
50	0·81	0·84	0·86	0·86	0·75	0·73
100	0·80	0·82	0·86	0·86	0·75	0·74
200	0·79	0·81	0·86	0·86	0·76	0·74
400	0·77	0·80	0·86	0·86	0·76	0·74
1000	0·75	0·77	0·85	0·86	0·76	0·74
2000	0·74	0·75	0·85	0·85	0·76	0·73

* In T., 1914, **105**, 2422 and 2423, the anodic overvoltage of platinum was given at 0·56 instead of 0·86. The error was unfortunately not observed until after publication.

Anodic Overvoltage in N-*Sulphuric Acid.*

Current Density.	*A.* Pb.	*B.* Pb.	*A.* Fe1.	*B.* Fe1.	*A.* Fe4.	*B.* Fe4.
2	0·80	0·91	0·73	0·75	0·70	0·70
4	0·83	0·94	0·74	0·75	0·78	0·78
6	0·85	0·96	0·74	0·76	0·82	0·80
10	0·88	0·98	0·75	0·75	0·85	0·81
20	0·91	0·99	0·74	0·75	0·87	0·82
50	0·95	1·04	0·74	0·74	0·88	0·82
100	0·98	1·05	0·73	0·73	0·88	0·82
200	1·00	1·06	0·72	0·73	0·87	0·82
400	1·01	1·06	0·71	0·70	0·85	0·81
1000	1·00	1·05	0·68	0·67	0·81	0·80
2000	0·98	1·04	0·63	0·63	0·78	0·78

Fe1 pure iron.
Fe4 "tantiron."

Anodic Overvoltage in N-*Sulphuric Acid.*

Current density.	*A.* Ni.	*B.* Ni.	*A.* C1.	*B.* C1.	*A.* C2.	*B.* C2.
2	—	—	0·25	0·45	0·75	0·67
4	—	—	0·32	0·53	0·84	0·69
6	—	—	0·37	0·57	0·88	0·71
10	—	—	0·43	0·61	0·91	0·75
20	—	—	0·52	0·66	0·94	0·81
50	—	—	0·71	0·77	1·00	0·88
100	0·62	0·62	0·85	0·83	1·05	0·92
200	0·65	0·65	0·90	0·87	1·08	0·96
400	0·67	0·67	0·91	0·91	1·12	1·01
1000	0·68	0·68	0·89	0·90	1·14	1·08
2000	0·68	0·68	0·88	0·88	1·14	1·10

C1 gas carbon.
C2 artificial graphite.

Anodic Overvoltage in N-*Sulphuric Acid. Time Experiments.*

Lead.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	−0·09	+0·44	0·59	0·62	0·62	0·61	0·61	0·61	0·61	0·61
10	0·93	0·93	0·94	0·95	0·96	0·99	0·99	0·99	0·99	0·99
100	1·02	1·04	1·06	1·07	1·07	1·07	1·07	1·07	1·06	1·06
1000	1·07	1·07	1·07	1·07	1·07	1·07	1·07	1·07	1·07	1·07

Iron.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·21	0·20	0·20	0·20	0·21	0·20	0·21	0·21	0·26	0·28
10	0·69	0·70	0·70	0·70	0·70	0·71	0·72	0·72	0·72	0·72
100	0·66	0·67	0·68	0·68	0·69	0·69	0·69	0·70	0·70	0·69
1000	0·66	0·66	0·66	0·66	0·66	0·66	0·66	0·67	0·67	0·67

Graphite.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·31	0·34	0·41	0·45	0·46	0·56	0·61	0·65	0·67	0·68
10	0·79	0·84	0·86	0·87	0·88	0·87	0·86	0·84	0·83	0·83
100	0·95	0·94	0·93	0·93	0·92	0·91	0·90	0·89	0·89	0·89
1000	1·02	1·01	1·00	0·99	0·98	0·97	0·96	0·96	0·96	0·96

Anodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Au.	*B.* Au.	*A.* Pt.	*B.* Pt.	*A.* Cu.	*B.* Cu.
2	0·71	0·96	0·56	0·85	0.53	0·57
4	0·76	0·96	0·57	0·86	0·57	0·61
6	0·87	0·96	0·59	0·87	0·59	0·62
10	0·91	0·96	0·62	0·87	0·61	0·63
20	0.92	0·96	0·72	0·88	0·62	0·63
50	0·93	0·96	0·75	0·99	0·62	0·62
100	0·94	1·01	0·80	0·98	0·62	0·61
200	0·94	1·16	0·82	0·97	0·61	0·60
400	0·93	1·20	0·85	0·94	0·60	0·59
1000	0·93	1·17	0·86	0·90	0·58	0·58
1200	0·93	1·16	0·85	0·88	0·58	0·57

Anodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Ag.	*B.* Ag.	*A.* Pb.	*B.* Pb.	*A.* Zn.	*B.* Zn.
2	—	—	0·60	0·86	—	—
4	0·10	0·60	0·64	0·93	—	—
6	0·35	0·69	0·66	0·94	—	—
10	0·36	0·70	0·69	0·95	—	—
20	0·58	0·71	0·82	0·96	0·83	0·87
50	0·60	0·72	0·83	0·96	0·85	0·97
100	0·63	0·72	0·84	0·95	0·91	1·00
200	0·65	0·73	0·84	0·94	0·94	1·00
400	0·70	0·72	0·86	0·93	0·93	0·96
1000	0·70	0·71	0·84	0·92	0·76	0·78
1200	0·69	0·69	0·83	0·90	—	—

Anodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* Ni.	*B.* Ni.	*A.* Co.	*B.* Co.	*A.* Sn.	*B.* Sn.
2	0·45	0·49	0·58	0·54	1·17	1·22
4	0·48	0·53	0·60	0·55	1·27	1·27
6	0·49	0·54	0·60	0·56	1·34	1·31
10	0·51	0·57	0·59	0·57	1·34	1·35
20	0·53	0·60	0·58	0·57	1·35	1·37
50	0·54	0·64	0·58	0·57	1·35	1·33
100	0·55	0·65	0·57	0·56	1·34	1·33
200	0·56	0·66	0·57	0·56	1·34	1·32
400	0·57	0·66	0·56	0·56	1·29	1·30
1000	0·57	0·65	0·54	0·55	1·25	—
1200	0·57	0·64	0·54	0·54	—	—

Anodic Overvoltage in N-*Sodium Hydroxide.*

Current density.	*A.* C1.	*B.* C1.	*A.* C2.	*B.* C2.	*A.* Fe1.	*B.* Fe1.	*A.* Fe4.	*B.* Fe4.
2	0·05	0·26	0·53	0·52	0·44	0·44	0·31	0·50
4	0·11	0·34	0·56	0·54	0·46	0·46	0·40	0·51
6	0·16	0·38	0·56	0·56	0·48	0·48	0·43	0·52
10	0·24	0·47	0·60	0·58	0·49	0·49	0·51	0·53
20	0·32	0·54	0·62	0·60	0·49	0·49	0·52	0·55
50	0·48	0·70	0·65	0·71	0·50	0·51	0·54	0·59
100	0·65	0·79	0·69	0·89	0·51	0·51	0·55	0·62
200	0·74	0·83	0·71	0·96	0·51	0·52	0·56	0·71
400	0·88	0·90	0·83	1·00	0·51	0·52	0·59	0·81
1000	0·90	0·88	0·96	0·97	0·51	0·52	0·92	0·88
1200	0·85	0·86	0·94	0·94	0·50	0·51	0·94	0·91

C1 Gas carbon.
C2 Artificial graphite.
Fe1 Pure iron.
Fe4 "Tantiron."

Anodic Overvoltage in N-*Sodium Hydroxide. Time Experiments.*

Lead.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·61	0·61	0·61	0·61	0·61	0·61	0·61	0·61	0·61	0·61
10	0·65	0·66	0·68	0·70	0·70	0·75	0·84	0·90	0·92	0·94
100	0·75	0·92	0·93	0·94	0·94	0·97	1·01	1·02	1·02	1·03
1000	0·93	0·95	0·97	0·98	0·99	1·00	1·00	1·00	0·99	0·99

Nickel.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·40	0·42	0·42	0·42	0·42	0·42	0·42	0·42	0·42	0·42
10	0·51	0·51	0·51	0·52	0·52	0·53	0·54	0·54	0·55	0·55
100	0·61	0·62	0·63	0·63	0·64	0·66	0·67	0·68	0·69	0·69
1000	0·67	0·68	0·69	0·69	0·69	0·70	0·71	0·72	0·72	0·72

Iron.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·51	0·51	0·52	0·52	0·52	0·5	0·53	0·53	0·53	0·53
10	0·54	0·54	0·54	0·54	0·54	0·55	0·55	0·55	0·55	0·55
100	0·55	0·55	0·55	0·55	0·55	0·56	0·56	0·56	0·56	0·56
1000	0·57	0·56	0·56	0·55	0·55	0·56	0·56	0·56	0·56	0·56

Anodic Overvoltage in N-Sodium Hydroxide.

Graphite.

Current density.	Time in minutes. 1	2	3	4	5	10	15	20	25	30
1	0·55	0·57	0·58	0·58	0·58	0·59	0·59	0·60	0·60	0·60
10	0·93	0·95	0·96	0·96	0·95	0·95	0·96	0·97	0·98	0·98
100	0·92	0·92	0·93	0·93	0·93	0·93	0·94	0·94	0·94	0·95
1000	0·82	0·84	0·84	0·84	0·84	0·84	0·83	0·83	0·83	0·82

Notes on Individual Electrodes.

Gold.—This metal has a high anodic overvoltage, and partly owing to this and partly to its softness it suffers badly from disintegration. In acid electrolyte the surface becomes rough and spongy, whilst in alkali at high current density small particles are broken off and fall through the liquid. In strong acid the metal is broken up in the form of small flakes or spangles, and in most cases the electrolyte is coloured green by finely divided gold particles.

The overvoltage in acid is steady and fairly constant, and the maximum is reached at a comparatively low current density (compare cathodic overvoltage maximum).

In alkali the overvoltage is much higher and the maximum occurs at a high current density. Also there is a sudden jump in the overvoltage when the current density is raised from 50 to 100 milliamperes per sq. cm. This jump occurs repeatedly and always at approximately the same current density, whether the latter is being raised or lowered, after the first series of readings.

Platinum.—This certainly approaches most nearly of all metals our conception of an ideal insoluble anode for all cases. In acid electrolyte its overvoltage after the first few minutes is almost unalterable, either by time or current density, and is high enough to effect very powerful oxidations. It is the only readily available metal capable of withstanding the action of the nitrate-ion or sulphate-ion in concentrated nitric and sulphuric acids, and for these and many other reasons the high cost is greatly to be regretted as militating against its employment on the large scale.

In alkali electrolyte the overvoltage resembles that of gold in that it rises slowly with time and also shows a sudden large rise when the current density is changed from 20 to 50 milliamperes per sq. cm.

Disintegration is only observable with difficulty in acid after long use at high current density, but in alkali the surface becomes coated with a velvety, black deposit after some weeks' use, and this black deposit is at once converted into grey platinum on heating.

Copper.—This metal shows no signs of passivity in acid, being strongly negative to an oxygen electrode at all current densities, but in alkali the passive state is readily produced.

Its overvoltage in the passive state is low for anodic overvoltage, and is also very constant, being affected but little by time or current density changes. The maximum is produced at fairly low current density—below 50 milliamperes per sq. cm. For these reasons it is a very suitable anode for moderated oxidations in alkali electrolytes, but it cannot be used for long periods owing to the fact that it is slowly attacked and deposited on the cathode. It appears to pass rapidly through the electrolyte when once liberated, since no precipitate was formed and no copper could be detected in solution at any time, although the platinum cathode was covered with a shining, adherent film of copper.

Silver.—At low current densities a silver electrode dissolved slowly in acid electrolyte, and the potential of the metal remained negative with respect to an oxygen electrode.

When the current density was raised to 50 milliamperes per sq. cm. the metal suddenly became passive, the change occupying a few seconds only. The back electromotive force rose by more than 1 volt and solution almost ceased. On lowering the current density to 20 milliamperes per sq. cm. the electrode slowly became active again, the potential falling steadily for five minutes. With a current density of 40 milliamperes per sq. cm. a very slow periodic rise and fall of potential was observed, consisting of a fairly rapid rise of about 0·6 volt for about thirty seconds, followed by a similar, but slow, fall for two and a-half minutes. Similar phenomena are observed with nickel, but the periods in this case are much shorter.

In alkali also, silver is attacked at low current densities, the surface being rapidly coated with black oxide and the electrolyte also being discoloured. Metallic silver is deposited on the cathode. Even at higher current densities when passivity is produced the black coating is still formed, and on reversing the current this spongy coating is reconverted into grey metallic silver which, contrary to the usual behaviour of spongy electrodes, shows almost the same cathodic overvoltage as the massive metal.

The anodic overvoltage is not high in acid or alkali, but a silver anode may be used for oxidations in some cases in the presence of substances which readily reduce silver oxide. The disintegration of the anode in such cases is considerably less than in pure electrolytes.

Zinc.—This is one of the most difficult metals to passivate. In the acid electrolyte it showed no signs of passivity at the highest

current density available. In alkali it only became passive after the passage of a high current density, and readily became active again when the current density fell below 20 milliamperes per sq. cm. A velvety, black coating forms on the surface, which, after passing the current for some hours, assumes an enamelled, blue appearance. This dark blue coating when scraped off gives an almost white powder. The metal slowly dissolves, even when passive, and deposits on the cathode in a spongy condition.

The overvoltage is high but variable, and the electrical resistance of the film coating is considerable, so that this metal is unlikely to be of any practical value as an insoluble anode.

Lead.—Both in acid and alkali, a lead anode rapidly becomes coated with dioxide at moderate current densities, but at all current densities it shows a strong positive potential to an oxygen electrode after the dioxide coating has formed. While the coating is forming, the overvoltage rises steadily and remains very constant at a high value when the coating attains a thickness approaching 0·1 mm.

Lead is therefore a very suitable electrode for very powerful oxidations in dilute sulphuric acid electrolyte. Gold and graphite are certainly capable of attaining a somewhat higher overvoltage at high current densities, but as these are both disintegrated under these conditions, a lead electrode is much to be preferred.

In alkali its use is attended with certain disadvantages owing to the formation of plumbates which may interfere with the course of a reaction. The solubility of the peroxide in alkali prevents the formation of the protective coating at low current densities, and hence under these conditions lead behaves as an active metal. With a current density of 100 milliamperes per sq. cm. the metal becomes passive in about forty seconds, whilst it requires about fifteen minutes with a current density of 10 milliamperes per sq. cm.

In the time experiments with lead in acid electrolyte, negative values were obtained for the first five minutes at the lowest current density. Only the last one of these is given in the table. The potential rose rapidly as soon as the metal was completely covered with a visible coating of dioxide.

In alkali the first two series of values could not be obtained if a clean lead surface was used. The series at the lowest current density was therefore taken directly after that at the highest without cleaning off the dioxide. Under these conditions the coating slowly dissolves, as shown both by the change in appearance and by the fall of electrical resistance. Before taking readings at a current density of 10 milliamperes per sq. cm., the electrode was passivated by a current of 100 milliamperes for one minute. Lead

is the only electrode so far examined which is passivated more easily in acid than in alkali.

Nickel becomes passive in dilute sulphuric acid when a current density of 100 milliamperes per sq. cm. is applied. If the current density is lowered to 50 milliamperes, the well known periodic passivation and activation are observed, being more easily produced with this than with any other metal.

The potential falls from about 0·6 volt (referred to a standard oxygen electrode) slowly at first and then very rapidly to a value of about −0·5 volt, immediately rising again to near the highest value. The lower limit is very uncertain as it is almost impossible to follow the rapid changes of potential with the usual overvoltage apparatus. The period of each "vibration" is usually from six to ten seconds, and the nature is such as to suggest strongly an alternate formation and breakage of a continuous protective film over the surface of the electrode.

In alkali pure nickel passivates at once, even at the lowest current densities. If the nickel contains a small percentage of copper, however, the passivity is only partial, and the nickel is dissolved and deposited in a black, sooty form on the cathode, leaving the copper adhering to what is left of the anode. For this reason, samples of nickel from different manufacturers may show widely differing resistance to disintegration. Pure nickel sheet, such as was used for these experiments, is very slightly attacked by anodic treatment even in fused alkali at temperatures approaching 300°, whilst a sheet of 0·5 mm. thickness containing 2 per cent. of copper is completely destroyed by a few hours' use in similar circumstances.

Good quality nickel plating stands as well, or even better, than nickel sheet.

The anodic overvoltage of nickel is low and fairly constant, and has similar values in acid and alkali.

Cobalt, unlike nickel, cannot be passivated in the dilute sulphuric acid used, although its potential approaches that of an oxygen electrode when a very high current density is used. It is possible that passivity might be attained with a current density of 5000 or 10,000 milliamperes per sq. cm. At 2000 milliamperes per sq. cm. it is still active. In alkali, passivity is produced immediately, and the overvoltage is much the same as that of nickel, although a slight tendency to fall with time is observed, whilst that of nickel tends to rise.

Iron.—In dilute sulphuric acid pure iron requires a high current density to passivate it. If the electrode is connected to the source of current in such a way that 1 ampere per sq. cm. flows as soon

as it is dipped into the acid, passivity is induced in about three seconds. If the electrode is placed in the acid first and the current then applied, sixty seconds are required before it becomes passive, whilst if the metal is allowed to dissolve with or without current for a minute or so, it is difficult to passivate the electrode at all, even with this high current density. Hence in measuring the anodic overvoltages given in the tables, readings at the highest current densities were taken first and the current then reduced. For the time experiments a current density of 1000 milliamperes per sq. cm. was applied for half a minute at the beginning of each series. From the results obtained, it appears that a current density of 1 milliampere per sq. cm. is barely sufficient to preserve the protective coating formed in this time, although if the passivating current is continued for a few minutes before reducing to 1 milliampere per sq. cm. the anodic overvoltage is very much higher (more than 0·7 volt), and is easily kept at that value by the small current flowing.

In alkali it was not necessary to adopt any of these methods, since passivity was induced in a few seconds even at the lowest current densities. The surface of the metal kept quite bright until a current density of 500 to 1000 milliamperes per sq. cm. was applied, and then it was slightly blackened. In acid the surface was brilliant so long as the metal was active, but immediately acquired a dull leaden appearance on passivation.

"Tantiron" passivates far more easily than pure iron, requiring only 5 milliamperes per sq. cm. to induce passivity in ten seconds in *N*-sulphuric acid. Even with a current density of 1 milliampere per sq. cm. it becomes passive, but very slowly.

Steel of high chromium content becomes passive in about two seconds in acid with a current density of 1 milliampere per sq. cm. This extreme readiness to passivate is probably intimately connected with the corrosion-resisting powers of this alloy (stainless steel).

The overvoltage of "tantiron" is somewhat higher than that of pure iron, whilst both electrodes show considerably higher overvoltages in acid than in alkali.

Tin.—In acid electrolyte, tin shows no signs of passivity, but readily becomes passive in alkali. At the same time a black coating is formed similar to that obtained with zinc. The nature of these black substances is under investigation. The electrical resistance of the coating is considerable, since an applied electromotive force of 8 volts only produced a current of 0·4 ampere per sq. cm.

The overvoltage rises to a very high value, and is very erratic. The apparent overvoltage is probably raised artificially to some

extent by the action of the badly conducting coating forming a small capacity condenser which is charged by the primary exciting current and then discharged through the potentiometer.

Carbon.—The overvoltages of graphite and gas carbon are very variable in both acid and alkali. In acid, that of graphite rises to a very high value at high current density and the electrode disintegrates rapidly. With gas carbon, the disintegration is still greater, whilst the overvoltage is lower. At low current densities the disintegration is very slight, especially with graphite, but the surface is softened and the whole electrode becomes very brittle. Little or no deposit appears on the cathode.

In alkali, even at the lowest current densities, a black deposit is produced on the cathode, but the disintegration of the anodes is much less. No visible change is produced at the anode after passing currents up to 100 milliamperes per sq. cm. for half an hour. With a current of 1000 milliamperes per sq. cm. a gas carbon electrode gradually disintegrates, the liquid is discoloured, and a shower of small carbon particles falls to the bottom of the vessel. Under similar treatment, a graphite electrode acquires a crystalline appearance and a few particles fall off, but there is very little discoloration of the electrolyte. The crystalline appearance is produced in acid or alkali at high current densities, and, after drying, microscopic examination reveals the fact that the finely divided material between the larger crystals has been carried away, leaving the crystals themselves almost untouched.

Other Electrodes not given in the Tables.

Mercury under anodic treatment shows a positive potential to an oxygen electrode in acid or alkali, but is rapidly attacked in both cases with the formation of grey mercurous sulphate and yellow hydrated mercuric oxide respectively. Amalgamated electrodes behave in a similar manner. Bubbles of oxygen breaking through the coating on the surface make the potential very erratic.

Antimony in acid or alkali electrolyte becomes coated with a black deposit (almost invisible in acid), which has a very high electrical resistance. The back electromotive force rises apparently without limit. After five minutes with an applied electromotive force of 8 volts, the back electromotive force exceeded 7 volts and the current density fell to 1 milliampere per sq. cm.

Bismuth behaves in the same way, but the coating in acid was white and thick, whilst in alkali it was almost invisible, only a slight bronze colour being perceptible.

Tungsten, under anodic treatment in dilute sulphuric acid, dissolves readily and shows no signs of passivity. The surface acquires a very brilliant, polished appearance. In alkali, it behaves in the same way as bismuth.

Aluminium in alkali becomes passive with a current density of 600 milliamperes per sq. cm., giving an anodic overvoltage of 0·95 volt. When the current density is reduced to 400 milliamperes per sq. cm. the overvoltage falls to 0·01 volt. Below this, the metal dissolves slowly. It cannot be passivated in sulphuric acid. A very thin, brass-coloured film forms on the surface of the passive metal and prevents the current density from rising above 600 milliamperes per sq. cm. with an applied electromotive force of 8·2 volts.

Magnesium cannot be passivated in acid, but in alkali at high current density it becomes passive suddenly and remains passive at all current densities afterwards, the anodic overvoltage rising to a high value (over 1 volt) at low current density.

Manganese may also be passivated in alkali, but dissolves slowly, at the same time forming manganate and permanganate.

Iridium has the lowest anodic overvoltage in acid of any of the electrodes tried, keeping very constant at all current densities at about 0·50 volt.

General Conclusions.

From the tables it will be seen that the anodic overvoltages as a whole are much higher than cathodic, and that none of the electrodes examined is capable of giving an anodic overvoltage of less than 0·4 volt for any length of time. Hence moderated oxidations are very difficult to obtain, and in the electrolytic treatment of organic compounds there is a tendency to give highly oxidised products or even to destroy the substance with formation of carbon dioxide. Gas carbon at low current densities is perhaps the most suitable anode in many cases for moderated oxidations, but even this tends to increase its overvoltage with time, although slowly. For small scale experimental work, iridium anodes may sometimes be used in acid electrolytes, as this has a low and constant anodic overvoltage (0·5 volt in *N*-sulphuric acid).

Nickel steel (containing 36 per cent. of nickel) has an anodic overvoltage in acid intermediate between that of pure iron and nickel, but it passivates with much greater ease than either, and is very resistant to the disintegrating action of the anions in acid or alkali. Chrome steel also passivates readily, but is more liable to disintegration and oxidation than nickel steel.

For general work the most suitable anodes appear to be for dilute sulphuric acid or sulphate solutions, lead; for chloride solutions,

graphite; for alkali solutions or fusions, pure nickel or high nickel steel.

Theoretical considerations of overvoltage and passivity will be dealt with in Part III. of this series.

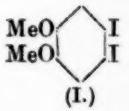
ELECTRO-CHEMICAL LABORATORIES,
MANCHESTER UNIVERSITY. [*Received, August 15th*, 1916.]

LXXVII.—*Experiments on the So-called Migration of Atoms and Groups. Part I. The Nitration of* p-*Iodoanisole and other Iodo-Phenolic Ethers.*

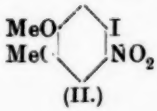
By GERTRUDE MAUD ROBINSON.

THE circumstances attending the migration of atoms and groups in chemical reactions or isomeric change are still but little understood, and it does not at present seem to be possible to include all such transformations in a single generalisation. In certain cases, such as the Beckmann rearrangement and the pinacone-pinacolin change, there appears to be no loophole of escape from the theory of the wandering atom, but it is quite possible that this is due to our limited knowledge of the possible intermediate stages. Orton and Jones (T., 1909, **95**, 1456) have shown that the migration of chlorine from side-chain to nucleus observed when *N*-chloroacetanilides are treated with hydrochloric acid is due to the formation of an acetanilide and chlorine, which interact with the formation of the end-product substituted in the nucleus together with regenerated hydrochloric acid. The clear proof, based on a study of the dynamics of the reactions involved, is convincing, and it is natural to group analogous reactions as also due to the intervention of intermediate stages, but it is not easy to realise the conditions in every case under which these phases may be studied. The present investigation has been undertaken in the hope that it will prove possible to apply the theory of successive reactions, the rational explanation of migration, to a number of transformations which at present do not appear to be capable of such elucidation. A large number of examples of migration of halogen atoms from one position to another in the aromatic nucleus have been noted, and the majority of these occur during the nitration or halogenation of phenols, and usually these changes may be readily explained

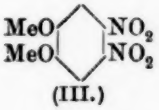
by the displacement of the halogen by the entering group and the re-entry by substitution in the new position. A curious reaction of this type was discovered by Reverdin (*Ber.*, 1896, **29**, 1003), who found that on nitrating *p*-iodoanisole the nitro-group displaces the iodine atom, which is apparently moved round to the ortho-position with respect to the methoxyl group. The difficulty presented by this example is that the further substitution of the *p*-nitroanisole, which may be assumed to be the initial product of the reaction, by the iodine also obtained, is, on the surface, improbable because *p*-nitroanisole is not very readily converted into derivatives by further substitution and, further, iodine is well known to be a somewhat inactive agent. However, experiment showed that iodine does react with *p*-nitroanisole in nitric acid solution with the formation of the iodo-*p*-nitroanisole obtained in the Reverdin transformation. It was also found that *o*-nitroanisole is changed by iodine in nitric acid solution to *p*-iodo-*o*-nitroanisole. As regards the first phase of the reaction the behaviour of iodo-phenolic ethers with nitric acid has been examined, and it is found that the normal reaction is the displacement of an iodine atom in the ortho- or para-position with respect to methoxyl with the formation of free iodine and a nitro-derivative. Thus 4:5-di-iodoveratrole (I) is changed successively to nitroiodoveratrole (II) and 4:5-dinitroveratrole (III), and 2:5-di-iodoquinol dimethyl ether exhibits a similar behaviour. 3-Iodo-6-nitro-*p*-tolyl methyl ether (IV) yields 3:6-dinitro-*p*-tolyl methyl ether (V), but in this case a by-product was found in 2:3:6-trinitro-5-hydroxy-*p*-tolyl methyl ether (VI):



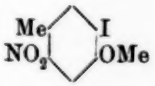
(I.)



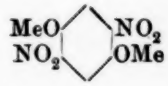
(II.)



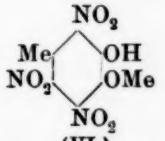
(III.)



(IV.)



(V.)

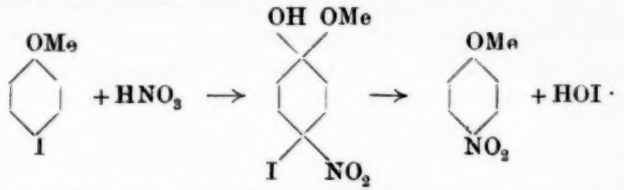


(VI.)

In other cases which have been examined the displacement of iodine is accompanied by further nitration or oxidation. It was not found possible to isolate *p*-nitroanisole from the interaction of *p*-iodoanisole and nitric acid, since conditions where the displacement was possible also favoured iodination or further nitration.

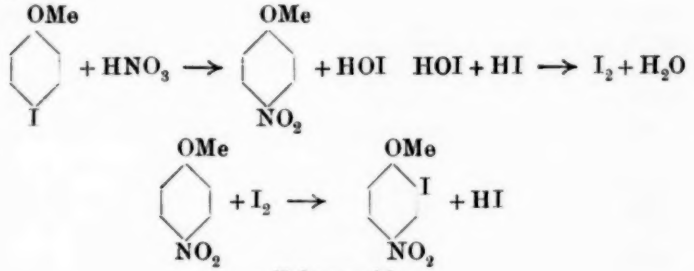
In considering the actual details of the mechanism of the reaction it is necessary, in the first place, to remember that the iodine is

probably removed from the nucleus in the form of hypoiodous acid, as shown in the scheme:



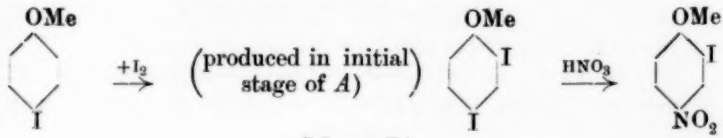
This then decomposes with the formation of iodine and iodic acid, and the latter substance was proved to be one of the products obtained when 4:5-di-iodoveratrole was treated with cold nitric acid (D 1·42).

It is possible, but not, in the author's opinion, very probable, that hypoiodous acid is the iodinating agent in the transformation, but it should be noted that iodine is observed to separate as such during the reaction, and this, acting on the nitroanisole, will produce a certain amount of hydrogen iodide which, in its turn, would be oxidised by any hypoiodous acid present. The following stages seem, therefore, to represent the more reasonable view of the process:



(Scheme *A*.)

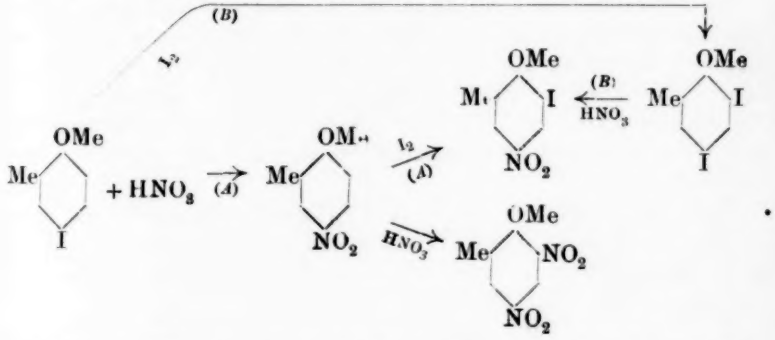
Although this process must occur to some extent, it is the author's opinion that the major proportion of the iodonitroanisole results from a process of iodination of the *p*-iodoanisole to di-iodoanisole, followed by displacement of the para-iodine atom and formation of *o*-iodo-*p*-nitroanisole. Di-iodoanisole can actually be isolated as an intermediate product of the reaction, and by further treatment with nitric acid is changed to the iodonitroanisole melting at 96°. These processes are represented in scheme B:



Scheme *B*.)

The remarks made in connexion with A relative to the displacement of nitroxyl and the substitution by means of iodine or hypoiodous acid apply also to the similar reactions in B.

The substituting action of iodine is not observed unless the nitric acid is of a sufficient concentration, and this consideration explains the limited scope of the transformation, since a rather peculiar state of affairs must be reached. The substance dissolved in the nitric acid must have a strongly positive group, since otherwise the iodine will not be displaced; and the product must not be nitrated further at the concentration of acid employed, but must be capable of iodination. Even with a substance so closely allied to *p*-iodoanisole as the corresponding *o*-cresol derivative the further nitration to a dinitro-compound occurs with inconvenient rapidity, and in order to observe the rearrangement it was found necessary to operate with great care. The reactions involved in this example are represented as follows:

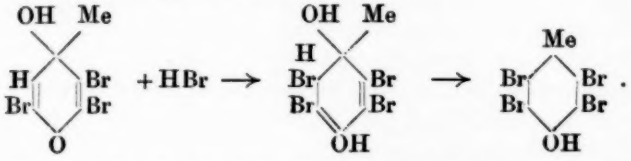


Other cases of migration of halogen atoms in phenols and their ethers will readily conform to the scheme of successive reactions and have in most cases been so represented, but Robertson and Briscoe (T., 1912, **107**, 1965), who have investigated transformations of this type especially among thymol derivatives, hold the contrary view. In certain examples of nitration of halogenated phenols, chlorine and bromine are displaced by nitroxyl, but remain in the molecule in a different position, whereas iodine is removed in the elementary condition, and it is supposed that the iodine is too heavy to reach the goal when it is displaced from its position.

It seems equally reasonable to assume that the iodine, once separated, does not re-enter the molecule because its reactivity is insufficient to effect the necessary substitution.

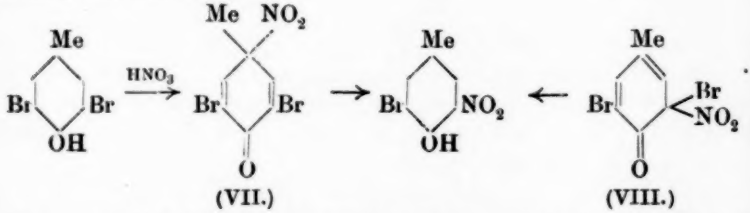
The views of Robertson and Briscoe are founded on those of Auwers, who has very generally assumed the fact of the migration of atoms and groups, basing his speculations on a considerable

series of experimental researches which cannot well be criticised *en masse*. Wanderings have been assumed to occur both to the adjacent carbon atom and to the next but one, and perhaps the theoretical difficulty presented by the assumption of a true leap may be somewhat less in the former than in the latter examples. The changes of the first class can very often be explained by an application of Thiele's theory of addition to conjugated systems, as shown below for the transformation of tribromo-ψ-quinol into tetrabromo-*p*-cresol under the influence of hydrobromic acid (Auwers and Dallwig, *Ber.*, 1902, **35**, 464):



As an example of migration to the next but one carbon atom the nitration of dibromo-*p*-cresol may be quoted, and this is the actual case which Robertson and Briscoe (*loc. cit.*) mention in support of their hypothesis. The experimental evidence adduced by Auwers (*Ber.*, 1902, **35**, 357) in support of his contention that the reaction should be represented as shown below seems far from conclusive.

The action of nitric acid on dibromo-*p*-cresol yields an intermediate hemi-*p*-quinone (VII), and under the influence of reagents the nitro-group is supposed to wander to the ortho-position, displacing the bromine atom:



(VII.) (VIII.)

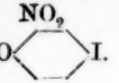
However, this hemiquinone (VII), the constitution of which is the key to the solution of the problem, does not undergo simple reactions resulting in a high yield of product, and has none of the characteristics of a pure substance. It melts over a range of temperature, and its unstable character is emphasised in the description. As likely as not, it contains the isomeric hemi-*o*-quinone (VIII), and probably the proportion of this in the product could be judged by the amount of bromonitrocresol obtained when the mixture is treated with alkali solutions. Both (VII) and (VIII) represent anhydrides of the initial product of addition of nitric acid

to dibromo *p*-cresol, and it is probable that an equilibrium is reached in neutral or acid solutions. Such considerations can account for the results obtained by Auwers and others in examining the nitration of phenols without the improbable assumption of the wandering of atoms or groups.

Experimental.

2-Iodo-4-nitroanisole.

The formation of this substance by the nitration of both *o*- and *p*-iodoanisole as described by Reverdin (*loc. cit.*) was confirmed, and in carrying out the reaction in the latter case, the separation of iodine was observed. The substance may also be obtained by the iodination of *p*-nitroanisole in nitric acid solution. *p*-Nitroanisole (1 gram) was mixed with nitric acid (2 c.c., D 1·4) and powdered iodine (1·3 grams, 1·5 mols.). After allowing to remain overnight at the ordinary temperature, water was added, the excess of iodine removed by sulphurous acid, and the solid collected and crystallised from alcohol. The colourless needles melted at 96°, and the melting point was not lowered when a specimen was mixed with 2-iodo-4-nitroanisole obtained by either of Reverdin's methods. This investigator obtained a substance melting at 73° by the nitration of *p*-iodoanisole under certain conditions, and to this he ascribed the constitution of the substance described in the next section. However, this material, melting at 73°, has been obtained and examined by the present author, and appears to be a mixture of 2-iodo-4-nitroanisole with either *p*-nitroanisole or more probably di-iodoanisole. The mixture is changed by nitric acid and iodine to pure 2-iodo-4-nitroanisole, melting at 96°. Many attempts, all unsuccessful, were made to isolate *p*-nitroanisole from the products obtained when nitric acid reacts with *p*-iodoanisole, but, on the other hand, the intermediate formation of di-iodoanisole was recognised. Nitric acid (D 1·5, 1 c.c.) was cooled in ice and *p*-iodoanisole (0·5 gram) added in one portion. The mixture was immediately flooded with water, neutralised, and distilled in a current of steam. The solidified oil was collected, crystallised from aqueous ethyl alcohol, and the substance obtained in colourless prisms melting at 68° alone or mixed with 2 : 4-di-iodoanisole. When this substance is treated with nitric acid the iodine in the *p*-position is displaced by nitroxyl, and the iodonitroanisole melting at 96° obtained along with free iodine.

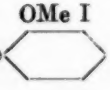
4-Iodo-2-nitroanisole, 

This substance was readily produced from *o*-nitroanisole exactly as described above for the iodination of *p*-nitroanisole. The substance crystallised from alcohol or acetic acid in pale yellow prisms melting at 98°. It may be distinguished from its isomeride, the subject of the last section, by its yellow colour. A mixture of the two compounds showed a depressed melting point:

0·1482 gave 0·1653 CO_2 and 0·0260 H_2O. C = 30·4; H = 1·9.

$C_7H_6O_3NI$ requires C = 30·2; H = 2·1 per cent.

The constitution of this substance is proved by its conversion, on treatment with fuming nitric acid, into 2:4-dinitroanisole melting at 88° (mixed melting point), and iodine, and also by the following transformation into 2:4-di-iodoanisole. The iodonitroanisole (3 grams) was reduced at the ordinary temperature during twelve hours by tin (3 grams) and concentrated hydrochloric acid (10 c.c.). The base was isolated by extraction with ether after the addition of sodium hydroxide and crystallised from alcohol in colourless plates melting at 87°. It was dissolved in dilute sulphuric acid, carefully diazotised, and the solution then added to an excess of an aqueous solution of potassium iodide. The product was dissolved in ether, freed from iodine by sulphurous acid, and crystallised from alcohol. The colourless prisms melted at 68—69°, and were identified as 2:4-di-iodoanisole (mixed melting point).

3-Iodo-o-tolyl Methyl Ether, 

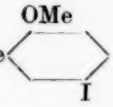
3-Nitro-*o*-tolyl methyl ether was obtained from the corresponding nitrocresol by a process of methylation which may successfully be applied for the preparation of the methyl ethers of mono-, di-, and even tri-nitrophenols. The ethers required for the present investigation were all prepared in this way, and in all cases with excellent results. The nitrophenol is heated in an oil-bath in boiling xylene solution with rather more than a molecular proportion of methyl sulphate and an excess of potassium carbonate. The reaction is finished when the red potassium salt has given place to colourless potassium sulphate and potassium methyl sulphate. The xylene is then removed by distillation in a current of steam. In certain cases, for example, in the methylation of picric acid, it is desirable to use nitrobenzene in place of the xylene.

3-Nitro-*o*-tolyl methyl ether was reduced and the amine con-

verted by diazotisation and treatment with potassium iodide in the usual manner into 3-*iodo*-o-*tolyl methyl ether*, an oil boiling at 200°/19 mm.:

0·1650 gave 0·1573 AgI. I = 51·5.

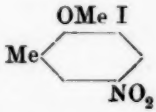
C_8H_9OI requires I = 51·2 per cent.

5-Iodo-o-tolyl Methyl Ether, 

The 5-amino-*o*-tolyl methyl ether required for the preparation of this substance crystallises from methyl alcohol in long, slender needles melting at 92—93°, whereas Hofmann and Miller (*Ber.*, 1881, **14**, 571) give 52—53°. Its acetyl derivative was prepared and crystallised from water or methyl alcohol in needles melting at 158°. The amine was converted into the corresponding diazonium sulphate, and the diazo-group then displaced by iodine in the usual manner. The 5-*iodo*-o-*tolyl methyl ether* was obtained in excellent yield. It crystallises from acetic acid in colourless plates melting at 79—80°:

0·1366 gave 0·1938 CO_2 and 0·0506 H_2O. C = 38·7; H = 4·1.

C_8H_9OI requires C = 38·7; H = 3·6 per cent.

3-Iodo-5-nitro-o-tolyl Methyl Ether, 

A. 3-Iodo-*o*-tolyl methyl ether (1 gram) was mixed with nitric acid (4 grams, D 1·4) and allowed to remain overnight. The solid precipitated by the addition of water was collected and crystallised from aqueous methyl alcohol and obtained in long, hair-like, colourless crystals melting at 83° and readily soluble in most organic solvents:

0·1559 gave 0·1891 CO_2 and 0·0428 H_2O. C = 33·1; H = 3·0.

$C_8H_8O_3NI$ requires C = 32·8; H = 2·7 per cent.

B. The nitration of 5-iodo-*o*-tolyl methyl ether under the same conditions resulted in the separation of iodine and the production of a relatively smaller yield of the nitro-derivative, which was always produced along with 3:5-dinitro-*o*-tolyl methyl ether, and separated by fractional crystallisation from aqueous methyl alcohol, and finally from methyl alcohol. A careful comparison and mixed melting-point determination showed that the product was identical with that described under *A*.

C. The combined action of nitric acid and iodine on 5-nitro-*o*-

tolyl methyl ether also resulted in the production of 3-iodo-5-nitro-*o*-tolyl methyl ether. The substance melted at 83° after crystallisation and the melting point was not depressed when the substance was mixed with a specimen obtained from 3-iodo-*o*-tolyl methyl ether.

When 3- or 5-nitro- or -iodo-*o*-tolyl methyl ether are treated with fuming nitric acid or heated with nitric acid, they all yield one and the same 3:5-dinitro-*o*-tolyl methyl ether, which crystallises from aqueous alcohol in nearly colourless needles melting at 71—72°. It may also be obtained by the nitration of *o*-tolyl methyl ether. The corresponding ethyl ether has been described by Städel (*Annalen*, 1883, **217**, 154), and this methoxy-derivative resembles it in yielding dinitrocresol, pale yellow needles melting at 85°, on hydrolysis with a boiling solution of sodium hydroxide (20 per cent.), whilst on heating in a sealed tube at 100° with ten times its weight of a mixture of equal volumes of methyl alcohol and aqueous ammonia (D 0·880) a sparingly soluble, yellow precipitate of 3:5-dinitro-*o*-toluidine was formed in three hours. The solid was collected and crystallised from acetic acid and obtained in yellow, prismatic needles melting at 214°. Städel (*Annalen*, 1883, **217**, 183) gives 208° and Bamberger and Seitz (*Ber.*, 1897, **30**, 1253) give 211°. This nitroamine remains unchanged in boiling acetic anhydride, but on the addition of a trace of sulphuric acid is rapidly acetylated with the formation of the colourless acetyl derivative which crystallises in needles and melts at 203°.

4:5-*Di-iodoveratrole and* 2:5-*Di-iodoquinol Dimethyl Ether.*

These substances have previously been prepared, the former by Brüggemann (*J. pr. Chem.*, 1896, [ii], **53**, 252) and the latter by Kauffmann and Fritz (*Ber.*, 1908, **41**, 4416), by the action of iodine and mercuric oxide on the corresponding phenolic ethers. The process is inconvenient and the yield poor, and in place of it the author has employed the following method: Veratrole or quinol dimethyl ether (15 grams) was mixed with acetic acid (20 c.c.) and a solution of iodine monochloride (26 grams) in acetic acid (20 c.c.) gradually added. After the initial reaction, accompanied by development of heat, had subsided, the mixture was heated on the steam-bath until no more hydrogen chloride was evolved. On cooling, colourless needles separated, and a further quantity could be obtained by the addition of water. The solid was collected and crystallised from alcohol containing sulphurous acid. Di-iodoveratrole melted at 132° (Brüggemann, *loc. cit.*, gives 125°), and the quinol derivative at 171°, as described by the authors mentioned above.

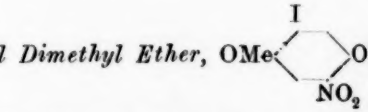
4-Iodo-5-nitroveratrole (Formula II).

Di-iodoveratrole (4 grams) was dissolved in acetic acid (125 c.c.) and nitric acid (40 c.c., D 1·4) gradually added. After fifteen minutes the product was precipitated by water and collected. It consisted of 4-iodo-5-nitroveratrole, which was obtained in almost theoretical amount. The substance was washed with sulphurous acid and water and crystallised from alcohol, in which it is sparingly soluble, in intense yellow needles melting at 151°:

0·1679 gave 0·1948 CO_2 and 0·0456 H_2O. C = 31·6; H = 3·0.

$C_8H_8O_4NI$ requires C = 31·1; H = 2·6 per cent.

On further treatment with nitric acid (D 1·4, mixed with 10 per cent. of D 1·52) the remaining iodine was displaced by nitroxyl and 4:5-dinitroveratrole formed. The substance melted at 129° alone, or when mixed with 4:5-dinitroveratrole obtained by direct nitration of veratrole.

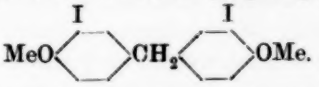
2-Iodo-5-nitroquinol Dimethyl Ether, 

Di-iodoquinol dimethyl ether was dissolved in the minimum amount of cold acetic acid and an equal volume of nitric acid (D 1·42) added. After fifteen minutes the product was separated by the addition of water, and as in the previous example the reaction had proceeded in almost quantitative manner with the formation of an iodonitro-derivative. The solid was collected, washed with sulphurous acid, and crystallised from alcohol, being so obtained in bright yellow needles melting at 152°:

0·0954 gave 0·1114 CO_2 and 0·0252 H_2O. C = 31·8; H = 2·9.

$C_8H_8O_4NI$ requires C = 31·1; H = 2·6 per cent.

When this substance is covered with fuming nitric acid and water immediately added, the second iodine atom is displaced and the substance after collection and crystallisation from alcohol melted at 200—202° and at the same temperature when mixed with a specimen of undoubted 2:5-dinitroquinol dimethyl ether.

3:3′-Di-iodo-4:4′-dimethoxydiphenylmethane, 

o-Iodoanisole (1 gram) was mixed with sulphuric acid (8 grams of 80 per cent.) and an aqueous solution of formaldehyde (1·5 grams of 40 per cent.) gradually added with cooling. After remaining

overnight the mixture was added to water, the solid collected, and crystallised from acetic acid, being obtained in plates melting at 142°:

0·1530 gave 0·1478 AgI. I=52·3.

$C_{15}H_{14}O_2I_2$ requires I=52·9 per cent.

The substance dissolves in concentrated sulphuric acid to a pale pink solution which becomes brown on warming.

An alternative method of preparation is from 3:3′-dinitro-4:4′-dimethoxydiphenylmethane (D.R.-P., 140690) by reduction with tin and hydrochloric acid, followed by tetrazotisation and displacement of the diazo-groups by iodine in the usual manner. The substance so obtained was identical with that described above.

The substance is either unacted on by nitric acid or, under more vigorous conditions, is changed to 2:4-dinitroanisole; no intermediate products could be isolated.

3-*Iodo*-6-*nitro*-p-*tolyl Methyl Ether* (Formula IV).

Nitro-*p*-cresol was smoothly converted into its methyl ether by the process previously described (see p. 1084) and the methoxy-derivative reduced at 50° by means of tin and hydrochloric acid. The amine isolated by distillation in a current of steam was crystallised from light petroleum (b. p. 60—70°) and obtained in feathery needles melting at 93—94°, whereas Hofmann and Miller (*Ber.*, 1881, **14**, 573) give 36—38° and Limpach (*Ber.*, 1889, **22**, 349) gives 51·5°. The acetyl derivative melts after crystallisation from alcohol at 107° (Limpach, *loc. cit.*, gives 110°), and on nitration yielded 6-nitro-3-acetylamino-*p*-tolyl methyl ether, yellow needles melting at 156° (Limpach, *Ber.*, 1889, **22**, 790). The nitroamine (15 grams), obtained by the hydrolysis of the acetyl derivative with concentrated hydrochloric acid and alcohol, was mixed with water (50 c.c.) and sulphuric acid (5 c.c.) and after cooling to 0° was gradually treated with sodium nitrite (2·1 grams) dissolved in water (25 c.c.). The yellow amine gradually passed into solution as the corresponding diazonium sulphate, and when the reaction appeared to be complete, the solution was filtered and added to potassium iodide (20 grams) dissolved in water (100 c.c.). The mixture was allowed to remain during a quarter of an hour, and the reaction then completed by warming on the steam-bath for a few minutes. Sulphurous acid was added to remove iodine, and the precipitate collected and crystallised from methyl alcohol, in which it is sparingly soluble in the cold. It was obtained in long, flat needles melting at 118°:

0·1141 gave 0·1355 CO_2 and 0·0314 H_2O. C = 32·4; H = 3·0.
$C_8H_8O_3NI$ requires C = 32·8; H = 2·7 per cent.

2:5-*Dinitro*-p-*tolyl Methyl Ether* (Formula V).

The iodonitro-*p*-tolyl methyl ether obtained as in the last section was mixed with three times its weight of fuming nitric acid, when the separation of iodine was observed. The solution was filtered through glass-wool and poured into water. The products were a neutral substance and a nitrophenol, and were separated by solution in ether and extraction of the latter by means of a 30 per cent. solution of potassium hydroxide. The bright red potassium salt separated in needles, and its examination is described later, whilst the ethereal solution was dried and the solvent removed by distillation. The crystalline residue was recrystallised from alcohol and obtained in pale yellow needles melting at 126°:

0·1101 gave 0·1851 CO_2 and 0·0394 H_2O. C = 45·8; H = 3·9.
$C_8H_8O_5N_2$ requires C = 45·3; H = 3·8 per cent.

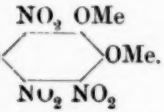
The relationship of this substance to the antecedent nitroamino- and iodonitro-compounds is shown by the following experiment, which proves that a direct displacement of iodine by nitroxyl has occurred. When either this substance melting at 126° or 6-nitro-3-amino-*p*-tolyl methyl ether was reduced by means of an excess of tin and hydrochloric acid and the resulting isolated base acetylated, the same diacetylamino-derivative was produced. The substance crystallised from alcohol, in which it is sparingly soluble, or from acetic acid, in long, slender, colourless needles melting at 270°:

0·1131 gave 0·2543 CO_2 and 0·0712 H_2O. C = 61·3; H = 7·0.
$C_{12}H_{16}O_3N_2$ requires C = 61·0; H = 6·8 per cent.

2:3:6-*Trinitro*-5-*hydroxy*-p-*tolyl Methyl Ether* (Formula VI).

The red potassium salt isolated as described above was dissolved in water and acidified with hydrochloric acid. The yellow, crystalline precipitate was found to be a mixture, and on crystallisation from aqueous alcohol and also from ether, the melting point gradually rose to 115°, when the substance appeared to be homogeneous. An analysis of a specimen of low melting point gave C = 37·2, H = 3·9, which indicates that the main product, a trinitro-compound, is contaminated with a similar dinitro-derivative. The substance melting at 115° occurred in yellow, rectangular prisms which dissolved in water to a yellow solution which gave insoluble, bright yellow precipitates with solutions of alkaloids, such as narcotine:

0·1091 gave 0·1408 CO_2 and 0·0326 H_2O. C = 35·2; H = 3·3.
$C_8H_7O_8N_3$ requires C = 35·1; H = 2·6 per cent.

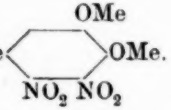
2 : 5 : 6-*Trinitrohomoveratrole*, 

The pure trinitro-compound just described was methylated by methyl sulphate in xylene solution in the presence of potassium carbonate, and after removing the solvent in a current of steam an oil remained which quickly solidified on cooling. It was collected and crystallised from aqueous methyl alcohol, and obtained in colourless needles melting at 73—74°:

0·1124 gave 0·1567 CO_2 and 0·0335 H_2O. C = 38·0; H = 3·3.
$C_9H_9O_8N_3$ requires C = 37·6; H = 3·1 per cent.

This substance remained unchanged when treated with a solution of nitric acid in sulphuric acid. It was converted into an orange-yellow nitroamine on boiling with concentrated alcoholic ammonia, but the product was not further examined.

Attempts were made to prepare this compound direct from homoveratrole or the known nitrohomoveratrole by further nitration, but without success, as the methyl group was always eliminated, probably by preliminary oxidation, followed by displacement of the formyl or carboxyl radicles produced. The result of nitration in sulphuric acid solution was always either 4 : 5-dinitroveratrole or, with more nitric acid, trinitroveratrole.

5 : 6-*Dinitrohomoveratrole*, 

This compound was prepared as a possible stepping-stone to the trinitrohomoveratrole. 6-Nitro-4-hydroxy-*m*-tolyl methyl ether (Cardwell and Robinson, T., 1915, **107**, 255) was dissolved in just sufficient sulphuric acid and nitrated by the addition of a little more than a molecular proportion of potassium nitrate. After remaining during a minute, ice was added, and the precipitated dinitro-derivative collected and dried. It was then methylated as in previous examples, and after removal of the xylene was dissolved in ether. The dried extract was evaporated, and the residue crystallised from aqueous methyl alcohol. The colourless needles so obtained melted at 120°:

0·0837 gave 0·1374 CO_2 and 0·0347 H_2O. C = 44·8; H = 4·6.
$C_9H_{10}O_6N_2$ requires C = 44·6; H = 4·1 per cent.

Attempts further to nitrate this substance were unsuccessful. On reduction and condensation with phenanthraquinone a deep yellow phenanthraphenazine was obtained. This dissolves in benzene to a yellow solution, which exhibits weak green fluorescence, and in sulphuric acid to a damson-red solution.

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[*Received, September 13th*, 1916.]

LXXVIII.—*Experiments on the Walden Inversion. Part IV. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid* —(continued).

By GEORGE SENTER and HARRY DUGALD KEITH DREW.

RATHER more than a year ago, a new chapter in the study of the Walden inversion was opened up by the discovery announced in our previous paper (T., 1915, **107**, 638) that optically active products of opposite sign may be obtained when the same reaction is carried out in different solvents. The particular reaction studied was the displacement of chlorine in ammonium phenylchloroacetate by the NH_2 group, as represented by the equation:
$C_6H_5{\cdot}CHCl{\cdot}CO_2NH_4 + 2NH_3 \longrightarrow C_6H_5{\cdot}CH(NH_2){\cdot}CO_2NH_4 + NH_4Cl$;
the phenylaminoacetic acid isolated from aqueous solution had the opposite sign to the chloro-acid taken, whilst the amino-acid isolated from acetonitrile had the same sign as the original acid. In both cases considerable racemisation occurred.

The present paper contains an account of further work on this subject. The action of ammonia on the active phenylchloroacetates has been examined in twelve different solvents, with the result that in six cases phenylaminoacetic acid having the same sign of rotation as the original chloro-acid was obtained, whilst in the remaining six cases the sign of the amino-acid was opposite to that of the original acid. The table on p. 1092 contains a summary of the results for reactions at the ordinary temperature. In the first and second columns the solvent used and the sign of the initial chloro-acid are given; the third column gives the specific rotation of the first crop of the amino-acid, which formed the bulk of the product, and in the fourth column the sign of the product is compared with that of the original chloro-acid.

TABLE I.

Solvent.	Sign of chloro-acid taken.	Specific rotation of amino-acid formed.	Comparison of sign of product and chloro-acid.
Liquid ammonia... ..	*l*-	−20°—90°	same sign
Water	*l*-	+83°	change of sign
CH_3·OH	*d*-	*d*- (very small)	same sign
C_2H_5·OH	*d*-	+24°	,,
C_3H_7·OH (*n*)	*d*-	+ 8°	,,
C_3H_7·OH (*iso*)	*d*-	+ 4°	,,
C_4H_9·OH (*n*)	*l*-	+ 3° (?)	change of sign
C_7H_{15}·OH (*n*)	*d*-	−73°	,,
C_6H_5·CH_2·OH	*l*-	+ 2°	,,
C_6H_5·CH_2·CH_2·OH...	*d*-	−16°	,,
CH_3·CN	*d*-	+ 6°	same sign
C_6H_5·CN	*d*-	− 4°	change of sign

Since the pure active acids have the rotations $[\alpha]_D^{20}$ ±157·8° (Fischer and Weichhold, *Ber.*, 1908, **41**, 1285) it is clear that the main bulk of the product from solutions in aqueous ammonia, liquid ammonia, and *n*-heptyl alcohol contains about 50 per cent. of pure *d*- or *l*-acid. The average specific rotations of the products from all the solutions are rather greater than the numbers given in the table owing to the fact that the precipitated amino-acid has to be washed with water to free it from ammonium chloride, and the optically active amino-acids are more readily soluble in water than the racemic acid (Fischer and Weichhold, *loc. cit.*). Thus, although the value of $[\alpha]_D$ for the main bulk of product from acetonitrile is only +6°, it was shown in the previous paper that the specific rotation of the much smaller second crop was +127·5°.

In the former paper it was pointed out that whereas in aqueous solution racemisation was greater the higher the temperature, no increase of racemisation was observed in acetonitrile on altering the temperature of reaction from 18° to 52°. It has now been found that when benzyl alcohol and benzonitrile are used as solvents, racemisation is greater at 52° than at 18°. In the case of liquid ammonia, however, increase of temperature does not appear to increase the racemisation; in fact, a rather more active product was obtained at 25° than at 10° (p. 1105).

As the results obtained with liquid ammonia are of particular interest on account of the fact that relatively active products of opposite sign are obtained from this solvent and from aqueous ammonia, the reaction in these two solvents was more fully investigated. It is very remarkable that the activity of the product is greatly dependent on the original concentration of the chloro-acid in liquid ammonia; thus from a solution containing 0·25 gram of *l*-phenylchloroacetic acid in 1 c.c. of liquid ammonia the amino-acid obtained was quite inactive, whilst from a solution containing 0·016 gram of the chloro-acid per c.c. the value of $[\alpha]_D$ for the

amino-acid was $-89°$ (p. 1104). On the other hand, alteration of the concentration of the chloro-acid in aqueous ammonia had very little effect on the activity of the resulting amino-acid.

In view of these results, the effect of ammonium chloride on the extent of racemisation, both in aqueous and liquid ammonia, and the effect of other salts on the racemisation in liquid ammonia, was examined. When the displacement in liquid ammonia was carried out in the presence of ammonium chloride (2 grams in about 14 c.c.) a practically inactive product was obtained, whereas under the same conditions, but in the absence of ammonium chloride, the value of $[\alpha]_D$ exceeded 70°. On the other hand, the previous addition of ammonium chloride to the solution in aqueous ammonia had no racemising effect; in fact, a slightly more active product was obtained in the presence of the salt (p. 1103). In liquid ammonia the addition of ammonium nitrate caused a very marked increase in racemisation; sodium nitrate in this solvent had also a considerable racemising effect, although less marked than the ammonium salt.

The above results show that the marked effect of concentration on the extent of racemisation in liquid ammonia is due, in part at least, to the racemising effect of ammonium chloride, one of the products of the reaction. It may be mentioned that a product of the same optical activity is obtained from liquid ammonia whether the solution is kept for six or thirty-six days before separating the amino-acid, so that the ammonium chloride formed in the course of the reaction has no racemising effect on the active amino-acid once the latter is formed.

As mandelic acid is one of the products of the action of aqueous ammonia on phenylchloroacetic acid, the effect of the previous addition of this compound on the nature of the product from liquid ammonia (which gives a product differing in sign from that obtained from aqueous ammonia) was examined. It was found, however, that the product had the same sign, and practically the same activity, as that obtained from a solution containing no mandelic acid.

A second product, in addition to the amino-acid, was isolated from certain of the solutions, more particularly from liquid ammonia. After the phenylaminoacetic acid (consisting of a mixture of *d*- and *r*-acid) had been separated from the solution obtained by the action of liquid ammonia on *d*-phenylchloroacetic acid, the residual aqueous solution (neutral to litmus) was found to be distinctly lævorotatory. When the solution was made slightly acid to Congo-red and allowed to remain for a day, a small amount of substance separated in short, transparent needles. It was shown

by analysis and from the behaviour of the product that it consisted of a mixture of *r*- and *l*-iminodiphenyldiacetic acid, $CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2H$, the racemic form of which was first prepared a few months ago by Schlezinger (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1183) by an entirely different method. The new acid is formed according to the equation:

$$2CHPhCl{\cdot}CO_2NH_4 + 3NH_3 \longrightarrow CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2H + 2NH_4Cl,$$

and is no doubt present in the solution as the ammonium salt. When aqueous ammonia, *n*-butyl alcohol, and *n*-heptyl alcohol were used as solvents, small quantities of the imino-acid were obtained, and in each case the product was opposite in sign to the chloro-acid taken. As these solvents were the only ones examined for the presence of the imino-acid, it is probably always formed in small amount when ammonia acts on phenylchloroacetic acid.

It is important to add that, as shown by a separate experiment, on evaporating an ammoniacal solution of *r*-amino- and *l*-imino-acids in the approximate proportion in which they are formed in the solutions examined, the amino-acid could be separated by the usual method and showed no activity, all the active imino-acid being present in the filtrate. It might at first sight appear that the possible formation of the imino-acid renders the results uncertain when the activity of the product is slight, but the result just described shows that an objection on this ground does not arise.

The properties of the imino-acid are described in a later section of the paper (p. 1106).

The general character of the results obtained with other solvents are sufficiently indicated by the summary in table I. Details regarding the nature of the product in each case are given in the experimental portion of the paper.

Discussion of Results.

The question at once arises as to whether the results just described can be interpreted by any of the theories of the Walden inversion hitherto put forward. The best known theories of this phenomenon are those proposed almost simultaneously by Fischer (*Annalen*, 1911, **381**, 123; 1912, **394**, 350) and by Werner (*Ber.*, 1911, **44**, 881). Taking as an example the action of liquid ammonia on ammonium α-bromopropionate, Fischer assumes the intermediate formation of an additive product from these two compounds by residual affinity; when the bromine separates in the ionised form the NH_2 group can either take the place of the latter, in which case there will be no change of configuration, or one of the other three groups may take the place vacated by that group, with the

result that inversion will have occurred. Werner's theory is somewhat similar, but rather more definite. According to the nature of the groups already present, the entering group may be attracted to one of the three faces of the tetrahedron (formed by the central carbon atom and the four associated groups) contiguous to the group, X, to be displaced, in which case no inversion occurs, or the entering group may be attracted to the face remote from X, in which case inversion will occur. According to Werner, the entering group is attracted by the central carbon atom, but, according to Fischer, the entering group is not necessarily attached to the carbon atom, but may be attached to one of the four substituents (compare Frankland, T., 1913, **103**, 721).

It will be seen that these theories are of very general character, and hitherto they have not proved of much value as guides in the study of the Walden inversion. For instance, the possible influence of the solvent in such processes is ignored both by Fischer and by Werner, and the results described in the present paper therefore form a very striking illustration of the inadequacy of the theories in question. In the course of a criticism of Fischer's theory, Biilmann (*Annalen*, 1912, **388**, 330) has pointed out the importance of elucidating the exact mechanism of the changes involved, and cites in this connexion the kinetic investigations of one of us (Senter, T., 1907, **91**, 460; 1909, **95**, 1827; 1910, **97**, 346; 1911, **99**, 95) on the mechanism of the displacement of halogens by other groups (compare also Gadamer, *J. pr. Chem.*, 1913, [ii], **87**, 312). It may be added that there appears to be considerable justification for Biilmann's criticism that Fischer's theory is little more than a description of the facts.

It is becoming more and more evident that a satisfactory explanation of the Walden inversion is not likely to be reached on the lines of the general theories of Fischer and of Werner, which carry us very little further, and that the valuable experimental results of Walden, Fischer, McKenzie, and others on the general character of the phenomena require to be supplemented by a more accurate study of the mechanism of the reactions involved. The present communication is intended as a further contribution to this aspect of the subject. As only very few reactions have so far been investigated from this point of view (compare Senter, *loc. cit.*; Holmberg, *Ber.*, 1912, **45**, 997; *J. pr. Chem.*, 1913, [ii], **87**, 456) it is premature to enter on a full discussion of the bearing of the results on the general interpretation of the phenomenon.

Coming now to the discussion of the results summarised in table I, it may be stated at once that some of these results are so remarkable and unexpected that no satisfactory explanation of them has

so far been found. Apart from water and liquid ammonia, eight alcohols and two nitriles were used as solvents, the choice of solvent being limited by the condition that the ammonium phenylchloroacetate should be completely soluble in the liquid used. The observations which more particularly require explanation are: (1) that whereas there is no change of sign with the four lower alcohols, a change of sign occurs when the reaction is carried out in *n*-butyl, *n*-heptyl, or benzyl alcohol and benzylcarbinol (β-phenylethyl alcohol); (2) that products of different sign are obtained from solvents normally so similar in behaviour as water and ethyl alcohol; (3) that products of different sign are obtained from aqueous ammonia and liquid ammonia; (4) that ammonium chloride has a markedly racemising effect in liquid ammonia, but not in aqueous ammonia.

Referring first to the results obtained with aqueous and with liquid ammonia, it may be noted that Fischer has incidentally investigated the displacement of halogen by the NH_2 group in aqueous and in liquid ammonia for three different compounds (*l*-α-bromopropionic acid ⟶ *l*-alanine and ethyl *l*-α-bromopropionate ⟶ *l*-alanine, *Ber.*, 1907, **40**, 491; *d*-α-bromo*iso*valeric acid ⟶ *l*-valine, Fischer and Scheibler, *Ber.*, 1908, **41**, 892), and in each case amino-acids of the same sign were obtained from the two solvents. It is probable that the different results obtained by Fischer and ourselves are connected with the fact that all the compounds examined by him belong to the aliphatic series, whereas we are concerned with an aromatic compound. So far as we are aware, no other aromatic compound has hitherto been examined from this point of view, but the displacement of halogen by the NH_2 group in phenylbromoacetic acid and β-phenyl-α-bromopropionic acid is now under investigation in this laboratory, and the question will be more fully discussed when the further data are available. At present it can only be suggested that the main reactions in aqueous and in liquid ammonia are different in character, and that this difference is conditioned in some way by the phenyl group. That the reactions in the two solvents are different in character is supported by the very different effect of ammonium chloride in the two cases.

The explanation of the results described might be attempted from two different points of view: (1) that in some solvents ammonia reacts mainly with the phenylchloroacetate ion and in others with non-ionised ammonium phenylchloroacetate, which might give rise to products of opposite sign; (2) that in some solvents free ammonia, in others combined ammonia (in association with the solvent), reacts with the phenylchloroacetate. At present the data are not sufficient to enable us to test the first suggestion adequately, and the second does not appear very promising. For instance, if the differ-

ence in sign of the products from aqueous and liquid ammonia is due to the fact that in the one case combined ammonia, in the other case free ammonia reacts, it is difficult to see why amino-acids of the same sign are obtained from these two solvents when active bromopropionic acid is used.

In water and the alcohols, besides the formation of amino-acids, simultaneous reactions occur, resulting in the formation of mandelic acid and alkyloxy-acids respectively, but there is no evidence that the formation of these products has any influence on the results.

The fact that acetonitrile and benzonitrile yield products of different sign is another illustration of the rule that in solvents of high molecular weight the product is usually formed with change of sign.

It has already been mentioned that whereas from *d*-phenylchloroacetic acid the *d*-amino-acid is obtained from liquid ammonia and the *l*-amino-acid from aqueous ammonia, the imino-acid isolated from both solvents is lævorotatory. At first sight it might appear that this fact throws some light on the mechanism of formation of the imino-acid. If *d*-phenylchloroacetic acid reacts equally fast with the *d*- and *l*-amino-acids, according to the equation:

$$NH_2\cdot CHPh\cdot CO_2H + Cl\cdot CHPh\cdot CO_2H \longrightarrow CO_2H\cdot CHPh\cdot NH\cdot CHPh\cdot CO_2H + HCl,$$

then it would clearly be impossible to obtain from the two solutions imino-acids of the same sign $\begin{pmatrix} d \\ | \\ d \end{pmatrix}$ or $\begin{pmatrix} l \\ | \\ l \end{pmatrix}$, since substitution does not take place at the asymmetric carbon atom belonging to the amino-acid (but only at the NH_2 group, which remains attached throughout to the central carbon atom), and therefore no Walden inversion can occur at this part of the molecule, and the arrangement of the groups in the imino-acids from the two solutions must necessarily be different. The fact that imino-acids of the same sign are actually obtained would then show that their formation does not take place through the intermediate formation of amino-acid, but probably by simultaneous reaction between two chloro-acid molecules and ammonia. The assumption, however, that *d*-phenylchloroacetic acid reacts equally fast with the *d*- and *l*-amino-acids is almost certainly erroneous; in fact, the method of asymmetric synthesis introduced by Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130) depends on the fact that in certain cases an optically active compound reacts at different rates with the *d*- and *l*-varieties of another compound. Marckwald and Meth (*Ber.*, 1905, **38**, 801), for example, have shown that *d*-mandelic acid is more quickly converted into amide by *l*-menthylamine than is *l*-mandelic acid. As in the present case both *d*- and *l*-amino-acids are always present owing to racemisa-

tion, the formation of excess of the same imino-acid in both solvents can be readily accounted for on similar lines.

Experimental.

Method of Experiment.

The method employed was to dissolve a weighed amount of the active chloro-acid in a measured volume of the solvent (usually 1 gram to about 15 c.c.); the solution was then saturated with dry ammonia, and left in a sealed tube for a definite period at the desired temperature.

In the case of ten out of the twelve solvents used, the bulk of the amino-acid was precipitated, together with a variable amount of ammonium chloride, as the reaction proceeded. The precipitate was collected, washed with ether to free it from traces of the solvent, and then treated with cold water until free from ammonium chloride. This gave a first crop of amino-acid. From the residual filtrate the excess of ammonia was expelled, and the solvent was removed as completely as possible (if necessary by distilling under diminished pressure), the residue was added to the washings from the first crop, and then excess of dilute hydrochloric acid was added. The resulting solution was extracted with ether to remove any unchanged chloro-acid and any non-basic acid formed during the reaction. The aqueous acid solution then contained the hydrochloride of any amino-acid which remained in the solvent after removal of the first crop. From this solution a small second crop of amino-acid was obtained by evaporating to dryness and neutralising the product with aqueous ammonia.

In the two cases (those of aqueous and liquid ammonia) in which no amino-acid was precipitated, the solvent was evaporated, the residue dissolved in dilute hydrochloric acid, the solution extracted with ether, and the amino-acid obtained as before.

The determinations of the rotation were carried out in all cases in 0·984*N*-hydrochloric acid. As the value of $[\alpha]$ depends to some extent on the concentration of the amino-acid, the value of c, in grams per 100 c.c., is given in each case. The observations were made at the ordinary temperature.

The nature of the product was established in all cases by determining the equivalent of the amino-acid, and in certain cases the results were checked by determinations of the proportion of nitrogen in the product. A convenient method of determining the equivalent is to convert the acid into the hydrochloride and note the increase in weight, the percentage of chlorine being then determined gravimetrically as a check. A weighed amount of the dried acid is dissolved in dilute hydrochloric acid, the water and excess of hydrochloric acid driven off by heating on a water-bath, and the

drying completed by heating for about an hour in the steam-oven. The drying must not be carried out at a temperature above 100°. As the method is very accurate, and the whole of the sample is taken for the experiment, a small amount of impurity in the amino-acid can readily be detected.

As an example, 0·1033 gram of the product from *n*-propyl alcohol gave 0·1284 gram of the hydrochloride (theory, 0·1283 gram), and the latter gave 0·0982 gram of silver chloride (theory 0·0980 gram). The products from the other solvents gave exactly comparable results, and it therefore appears unnecessary to quote them in detail.

Methyl Alcohol.

Preliminary experiments with *r*-phenylchloroacetic acid in this solvent showed that after seventy hours at 52° only about 2 per cent. of the chlorine is displaced by methyl alcohol alone, and that the presence of ammonia accelerates the displacement of the chlorine to a degree only partly accounted for by the formation of amino-acid. Thus in methyl alcohol saturated with ammonia 70 per cent. of the chlorine was displaced after forty-eight hours at 52° and 88 per cent. after one hundred and forty hours, although the proportion of amino-acid formed was less than 10 per cent. The probable explanation is that in the absence of ammonia the hydrochloric acid formed according to the equation:

$$Cl\cdot CHPh\cdot CO_2H + CH_3\cdot OH \longrightarrow CH_3\cdot O\cdot CHPh\cdot CO_2H + HCl,$$

retards the reaction to an even greater extent than in aqueous solution (compare Senter, T., 1915, **107**, 908).

Experiments were carried out at 15° and at 52° with solutions containing 1 gram of *d*-phenylchloroacetic acid in 15 c.c. of methyl alcohol saturated with ammonia. At the lower temperature the solution was kept for forty-two days. The first crop (0·08 gram) was inactive; from the aqueous filtrate a second crop (0·0074 gram) was obtained, which for $c=0·074$ gave for $[\alpha]_D$ the value $+74°$. The total yield of amino-acid was 10 per cent. The ethereal solution on evaporation gave a strongly dextrorotatory, oily mixture of acids (mainly phenylmethoxyacetic acid), which contained some unchanged chloro-acid.

The amino-acid obtained from the solution at 52° was quite inactive.

Ethyl Alcohol.

One gram of *d*-phenylchloroacetic acid in 20 c.c. of ethyl alcohol saturated with ammonia was kept for one hundred and twenty days at 15°.

The first crop (0·26 gram), $c=2·240$, had $[\alpha]_D$ $+24°$; the second crop (0·0175 gram), $c=0·175$, had $[\alpha]_D$ $+95°$. The total yield of

amino-acid was 32 per cent. The higher yield of amino-acid, as compared with that from methyl alcohol, is doubtless due to the fact that ethyl alcohol reacts less rapidly with the chloro-acid than does methyl alcohol.

The ethereal solution left an oil which was strongly dextrorotatory and probably contained some unchanged chloro-acid.

n-*Propyl Alcohol.*

One gram of *d*-phenylchloroacetic acid in 20 c.c. of *n*-propyl alcohol was kept for one hundred and twenty-three days at 15°.

The first crop (0·15 gram), $c=1·449$, had $[\alpha]_D$ +8°; the second crop, which was very small, was also dextrorotatory. The yield of the amino-acid was 17 per cent.

The ethereal solution on evaporation left a semi-solid residue. After conversion of the unchanged chloro-acid to *r*-mandelic acid by treatment with boiling sodium hydroxide solution (McKenzie and Clough, T., 1908, **93**, 811), acidification with hydrochloric acid, and extraction with ether, a dextrorotatory product was obtained. It appears, therefore, that phenylpropoxyacetic acid is formed from *n*-propyl alcohol and active phenylchloroacetic acid without change of sign

iso*Propyl Alcohol.*

One gram of *d*-phenylchloroacetic acid in 20 c.c. of *iso*propyl alcohol saturated with ammonia was kept for one hundred and twenty-nine days at 15°.

The first crop (0·34 gram), $c=1·592$, had $[\alpha]_D$ +4·4°; the second crop, which was very small, was also dextrorotatory. The yield of amino-acid was 39 per cent. The formation of amino-acid took place much more rapidly than in *n*-propyl alcohol, and this doubtless accounts for the smaller yield of amino-acid under similar conditions in the latter solvent.

n-*Butyl Alcohol.*

Two experiments were made in this solvent, 1 gram of active phenylchloroacetic acid in 15 c.c. of the alcohol saturated with ammonia being kept for fifty-two and one hundred and ninety-two days respectively at 15°. In the first experiment, with the *l*-chloro-acid, the first crop (0·09 gram), $c=0·844$, had $[\alpha]_D$ +3°, and the second crop, which was very small in amount, was also dextrorotatory. In the second experiment, for which the *d*-chloro-acid was used, both the first crop (0·35 gram) and the aqueous washings were quite inactive. The alcoholic filtrate from the first crop on evaporation under diminished pressure left a small residue which was acidified with hydrochloric acid and extracted several

times with ether. The aqueous portion was evaporated to dryness and the residue treated with aqueous ammonia as usual, but only a trace of amino-acid was obtained. The neutral aqueous solution was made just acid with hydrochloric acid, and on keeping a small quantity of a compound, which was later shown to be iminodiphenyldiacetic acid, separated in colourless needles. The value of $[\alpha]_D$ for this compound, $c=0{\cdot}118$, was $-140°$.

There is therefore a little uncertainty as regards the sign of the amino-acid obtained from *n*-butyl alcohol, as it is possible, although not probable, that the slight activity of the product in the first experiment was due to a trace of imino-acid.

n-*Heptyl Alcohol.*

One gram of *d*-phenylchloroacetic acid in 15 c.c. of *n*-heptyl alcohol (b. p. 174—176°) was kept for eighty-one days at 15°.

The first crop (0·10 gram), $c=0{\cdot}936$, had $[\alpha]_D$ $-73°$; the second crop (0·02 gram), $c=0{\cdot}200$, had $[\alpha]_D$ $-110°$. The total yield of amino-acid was 10 per cent. It is probable that the reaction was not nearly complete.

The filtrate from the second crop yielded a small quantity (0·01 gram) of imino-acid, which gave for $[\alpha]_D$ the value $-136°$, $c=0{\cdot}110$. The acid melted at about 202° (decomp.).

Benzyl Alcohol.

One gram of *l*-phenylchloroacetic acid in 15 c.c. of benzyl alcohol was kept for eighty-one days at 15°.

The first crop (0·27 gram), $c=2{\cdot}506$, had $[\alpha]_D$ $+2°$; the second crop (0·08 gram), $c=0{\cdot}078$, had $[\alpha]_D$ $+38°$. The total yield of amino-acid was 32 per cent.

A similar solution was kept for sixty-five hours at 52°. The first crop (0·3 gram) proved to be quite inactive.

Benzylcarbinol.

One gram of *d*-phenylchloroacetic acid in 15 c.c. of benzylcarbinol, b. p. 212° (saturated with ammonia), was kept for seventy-nine days at 15°.

The first crop (0·23 gram), $c=1{\cdot}266$, had $[\alpha]_D$ $-16°$; the filtrate gave only an extremely small quantity of amino-acid.

Acetonitrile.

The results with this solvent were described in our former paper, and are quoted in table I for the sake of completeness.

The following observations of the rotation in acetonitrile were made, because it was thought possible that phenylchloroacetic acid might form a compound with acetonitrile or with an ammoniacal

solution of this solvent, and that the presence of such a compound might be indicated by some abnormal effect on the specific rotation.

The specific rotation of *l*-phenylchloroacetic acid in acetonitrile has the following values for $c = 2{\cdot}258$ gram in 100 c.c.:

$[\alpha]_{\text{Hg green}}$ $-199°$, $[\alpha]_{\text{yellow}}$ $-172{\cdot}5°$, $[\alpha]_{\text{D}}$ -164,

as compared with those in benzene for $c = 3$ grams per 100 c.c.:

$[\alpha]_{\text{Hg green}}$ $-222°$, $[\alpha]_{\text{Hg yellow}}$ $-193°$, $[\alpha]_{\text{D}}$ -185.

On keeping for twenty-four hours the rotation of the acetonitrile solution was practically unchanged, $\alpha_{\text{Hg green}}$ being $-8{\cdot}98°$ for $l = 2$ dcm., but about three minutes after passing dry ammonia into the solution $\alpha_{\text{Hg green}}$ had fallen to $-8{\cdot}60°$ and after seventy-two hours to $-3{\cdot}20°$. There appears, therefore, to be no abnormal effect on the rotation which might indicate the formation of a compound with the solvent.

Benzonitrile.

One gram of *d*-phenylchloroacetic acid in 20 c.c. of benzonitrile was saturated with dry ammonia at 60° (because at lower temperatures the mixture formed a jelly) and kept for sixty-five hours at 52°. The amino-acid formed (0·34 gram) was quite inactive. Yield, 34 per cent.

A similar solution, also saturated with dry ammonia at 60°, formed a jelly on cooling. This was kept for one hundred and ninety-seven days, by which time the jelly had become opaque owing to the separation of a small quantity of precipitate. The amino-acid was separated in the usual way. The first crop (0·12 gram), $c = 1{\cdot}085$, had $[\alpha]_{\text{D}} -3{\cdot}7°$; the second crop (0·0114 gram), $c = 0{\cdot}114$, had $[\alpha]_{\text{D}} -70°$. The total yield of amino-acid was 15 per cent. The reaction appears to proceed very slowly in the jelly.

Separate experiments showed that a jelly could be obtained by passing dry ammonia into a solution of an active phenylchloroacetic acid (1) in acetonitrile when the concentration of the acid is greater than about 0·1 gram per c.c., (2) in benzonitrile when the concentration of the acid is greater than about 0·05 gram per c.c., the initial temperature of the solution being about 20°. At concentrations below these, the solutions remain clear, whilst at higher concentrations ammonium phenylchloroacetate seems to be formed as a precipitate. It appears probable that the jelly is a mechanical mixture of very finely divided ammonium phenylchloroacetate and the nitrile, for, when spread on a porous tile, the jelly seems slowly to lose the nitrile and a white, crystalline deposit of the salt remains.

Aqueous Ammonia.

It was stated in the previous paper that when the reaction was carried out in aqueous ammonia, using *l*-phenylchloroacetic acid,

the first crop of amino-acid had for $[\alpha]_D$ the value $+83°$ and the second crop the value $+135°$. The effect of altering the concentrations of ammonia and of phenylchloroacetic acid respectively, and the influence of ammonium chloride on the reaction, have now been investigated.

Variation in Concentration of Chloro-acid.—In each case 0·35 gram of *l*-phenylchloroacetic acid was dissolved in varying quantities of aqueous ammonia (D 0·880; $NH_3=35$ per cent.), and the solutions kept for about twenty days at the ordinary temperature. The results were as follows:

Concentration of chloro-acid (grams per 100 c.c.)	0·21	4·1	11·7
$[\alpha]_D^{20}$ of amino-acid	$+67°$	$+68°$	$+71·5°$

Hence an alteration in the concentration of the chloro-acid in aqueous ammonia appears to be almost without influence on the amount of racemisation in the formation of the amino-acid.

Variation in Concentration of Ammonia.—In this series of experiments the amount of *l*-phenylchloroacetic acid per unit volume of the solution was kept practically constant (0·5 gram in about 13 c.c. of solvent), but the relative proportions of water and ammonia were varied. The results were as follows:

Concentration per cent. of ammonia by weight	100	93·9	55·6	35
$[\alpha]_D$ of amino-acid	$-74°$	$-61°$	±0	$+68$

As products of different sign are obtained from aqueous ammonia and liquid ammonia, there must necessarily be a solution, containing between 35 and 100 per cent. of ammonia, which gives an inactive amino-acid. As shown in the table, the solution with this property contains 55·6 per cent. of ammonia. The proportions of nitrogen in the amino-acids from 93·9 per cent. and 55·6 per cent. ammonia were determined. The former was found to contain 9·4 per cent. and the latter 9·35 per cent. (theory requires N = 9·3 per cent.).

Effect of Ammonium Chloride.—Half a gram of *d*-phenylchloroacetic acid and 2 grams of ammonium chloride were dissolved in 12 c.c. of aqueous ammonia (35 per cent.) and the mixture kept for nineteen days at the ordinary temperature. The first crop of amino-acid (0·16 gram), $c=1·025$, had $[\alpha]_D -114·6°$, whilst an exactly corresponding experiment, but without the ammonium chloride, gave an amino-acid with $[\alpha]_D +68°$ for $c=0·661$. Although the ordinary temperature was rather higher in the latter case than in the former, the difference is much too great to be accounted for in this way, and it follows that there is less racemisation in the presence of ammonium chloride. From the solution to which ammonium chloride had been added a small quantity of imino-acid was isolated; it gave for $[\alpha]_D$ the value $-158°$, for $c=0·184$; m. p. (decomp.) 206—208°.

In a similar experiment in which the solution was kept for sixty-

five hours at 52°, the amino-acid formed was quite inactive, as was the acid formed under corresponding conditions in the absence of ammonium chloride.

Liquid Ammonia.

The experiments with this solvent were carried out as follows. A glass tube containing a weighed amount of the chloro-acid was immersed in a mixture of solid carbon dioxide and ether, and ammonia from a cylinder, after passing up a soda-lime tower, was led into the tube, where it condensed. The tube was then sealed and the temperature allowed to rise to that of the room. At low temperatures ammonium phenylchloroacetate was only partly soluble in liquid ammonia, but as the temperature rose, complete solution occurred. It was found that the reaction was practically complete in seven days at the ordinary temperature. The amino-acid was isolated in the usual way after the ammonia had evaporated. The effect of varying the concentration of the chloro-acid, and of the addition of various salts, was examined, and the influence of other variations of the experimental conditions on the nature of the product was investigated.

Variation in Concentration of Chloro-acid.—Solutions of the following amounts of *l*-phenylchloroacetic acid in definite volumes of liquid ammonia were left for seven days at the ordinary temperature and the amino-acid examined: 0·25 gram in 15 c.c.; $[\alpha]_D$ for first crop of 0·12 gram, $c=1·086$, was $-89°$; 0·5 gram in 14 c.c., $[\alpha]_D$ for first crop (0·28 gram), $c=0·976$, was $-77·4°$; 1 gram in 8 c.c., $[\alpha]_D$ for first crop (0·45 gram), $c=1·088$, was $-19·7°$; 0·25 gram in 1 c.c., the amino-acid (0·11 gram), $c=1·048$, was quite inactive. The results are summarised in the accompanying table:

Concentration of chloro-acid (grams per 100 c.c.)	25	12·5	3·6	1·6
Specific rotation of first crop	±0	−20	−77°	−89°

Effect of Ammonium Chloride and other Salts.—Half a gram of *l*-phenylchloro-acid and 2 grams of ammonium chloride were dissolved in liquid ammonia (12 c.c.) and the solution kept for seven days at the ordinary temperature. The amino-acid formed (0·30 gram) was inactive, whereas in the absence of ammonium chloride the value of $[\alpha]_D$ is about $-77°$. It is clear from this result that the increased racemisation with increased concentration of the chloro-acid is due, in part at least, to the racemising effect of the ammonium chloride formed in the course of the reaction.

From a solution containing 1 gram of ammonium nitrate in 8 c.c. of liquid ammonia the first crop of amino-acid was inactive, but the aqueous solution had the same sign as the original chloro-acid. From a similar solution, to which 0·12 gram of ammonium nitrate

had been added, the amino-acid gave for $[\alpha]_D + 64°$, $c = 1{\cdot}298$, whereas in the absence of the salt the specific rotation would have been about 79°.

The addition of sodium nitrate (1 gram) reduced the specific rotation of the first crop of amino-acid from about 79° to 12·4°. This salt has therefore a specific racemising effect, although much less marked than the corresponding ammonium salt. It may be mentioned that in this case sodium chloride gradually separated as the reaction proceeded.

The addition of mandelic acid (0·1 gram) to 8 c.c. of a solution in liquid ammonia resulted in the formation of an amino-acid with $[\alpha]_D + 69°$ for $c = 1{\cdot}094$, whereas in the absence of the acid the specific rotation would have been about 79°. The slight racemising effect is probably due to increased concentration of ammonium salt (ammonium mandelate), and not to a specific action of the mandelic group.

A solution of 0·25 gram of *d*-phenylchloroacetic acid in 7·5 c.c. of liquid ammonia, which had been kept for thirty-six days, gave a product of specific rotation +79°, identical with that from a solution kept for seven days, so that the active amino-acid is stable once it is formed. From a similar solution which had been kept for only one day the amino-acid (0·03 gram) gave for $[\alpha]_D$ a value of 62·5°, $c = 0{\cdot}280$, which is rather less than would have been anticipated.

The effect of alteration of temperature on the activity of the product was also examined. A solution of 0·25 gram of the *l*-acid in 7 c.c. of liquid ammonia was kept at 25° for seven days, and the first crop of amino-acid (0·11 gram) gave for $[\alpha]_D$ the value −88°, as compared with about −77° when the reaction took place at 12°. The temperature range is rather small, but the results show that, contrary to what occurs in aqueous ammonia, rise of temperature does not markedly influence the extent of racemisation in liquid ammonia.

The remarkable differences thus shown to exist between the reactions in aqueous and in liquid ammonia have been discussed in a previous section (p. 1096).

The proportion of nitrogen in several of the specimens of amino-acid obtained from solutions in liquid ammonia were examined. In all cases about 9·4 per cent. was found to be present (theory requires N = 9·3 per cent.).

Iminodiphenyldiacetic Acid.

The method by which a mixture of *r*- and *l*-iminodiphenyldiacetic acid was obtained from a solution formed by the action of liquid

ammonia on *d*-phenylchloroacetic acid has already been briefly described (p. 1093). In order to obtain sufficient of the *i*-acid for examination, 4 grams of *r*-phenylchloroacetic acid were dissolved in 15 c.c. of liquid ammonia and the solution kept for seven days. More than 3 grams of amino-acid were separated in the usual way, and from the neutral filtrate about 0·3 gram of the required compound was precipitated by means of dilute hydrochloric acid. The compound is acid to litmus, sparingly soluble in water, soluble in aqueous ammonia and in a large excess of hydrochloric acid, and it dissolves readily in an aqueous solution of sodium carbonate, with evolution of carbon dioxide. The aqueous solution gives an intense bluish-green solution on adding a drop or two of a very dilute solution of copper sulphate, and a solid, greenish-blue copper salt was also obtained. After crystallisation from hot water the imino-acid melted and decomposed at 196—197°.

After drying in the steam-oven at about 90° for many hours 0·4170 gram of the acid gave 17·95 c.c. N_2 (moist) at 21° and 759 mm., N = 4·89, as compared with 4·91 per cent. calculated for the anhydrous imino-acid. On keeping in moist air, however, the substance appears to take up a molecule of water. It was found that 0·1904 gram of the acid which had been exposed to moist air for some days weighed 0·1787 gram after heating at 110—130°, the calculated weight for one molecule of water eliminated being 0·1784 gram. The substance showed a faint yellow tinge, and on again leaving in moist air for a day the weight became 0·1857 gram. On now heating for an hour in the steam-oven the weight became once more 0·1789 gram.

From these results there appears to be no doubt that the substance is identical with the iminodiphenyldiacetic acid recently prepared by Schlezinger (*loc. cit.*) by hydrolysis of the nitrilo-ester, $CN{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2Et$. According to Schlezinger, the acid was obtained as the monohydrate from hydrochloric acid solution in spherical aggregates of slender needles or opaque nodules; it became anhydrous on heating at 120°, and on heating in a sealed capillary tube decomposed in the neighbourhood of 199°. In other respects also its behaviour corresponds with that shown by the imino-acid described above.

In conclusion, we desire to thank the Government Grant Committee of the Royal Society for a grant, part of which has been used to defray the expenses of this investigation.

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[*Received, October 4th,* 1916.]

LXXIX.—*Overvoltage Tables. Part III. Overvoltage and the Periodic Law.*

By Edgar Newbery.

The electrodes described in Part I. of this series were chosen originally with the idea of assisting the research chemist in his choice of electrodes for certain oxidations and reductions.

On studying the figures obtained, it soon became evident that the cathodic overvoltage of a metal was closely connected with its position in the periodic system. In order to examine this phenomenon still further, it became necessary to determine the overvoltage of as many metals as possible quite apart from their application to general electrolytic work. Ten more electrodes were therefore examined, and the results are given in the additional tables on pp. 1108, 1109. As before, column *A* represents the first set of readings taken with each electrode, whilst column *B* represents the average of at least four sets of readings.

In comparing the overvoltages of the various metals the chief difficulty lies in choosing the most representative values out of those found. The distinction between normal and abnormal values can only be arrived at by a careful study of each electrode under as many different conditions as possible. Two sets of controlling forces appear to be at work, one of which produces small variations within somewhat narrow limits, whilst the other produces such large variations as to amount to a complete change in the order of the values obtained. In some cases these two effects are clearly marked off, and there is then no difficulty in deciding upon the typical values. Such behaviour is observed with iridium, where four clearly marked stages occur, with sudden rapid changes from one to the other. In other cases, thallium in acid, for example, only one value is obtained with slight variations through a complete series of readings in a given electrolyte. Here, again, there is no difficulty in deciding on the typical overvoltage. In many cases, however, the effects of the two sets of forces are so confused that although great changes of overvoltage occur, no clearly marked stages can be recognised. Fortunately this seldom occurs in both acid and alkali, and even when it does, there are generally quite definite maximum and minimum values which correspond with the typical overvoltages of different groups.

Values for cathodic overvoltage in acid are usually more trustworthy than those in alkali, since in the former electrolyte only one cation is present, whilst in the latter two are possible. Values obtained in alkali are frequently of a higher order than can be

Cathodic Overvoltages in N-*Sulphuric Acid.*

Current density.	*A.* Cd.	*B.* Cd.	*A.* Tl.	*B.* Tl.	*A.* Ta.	*B.* Ta.	*A.* Cr.	*B.* Cr.	*A.* Mo.	*B.* Mo.	*A.* Mn.	*B.* Mn.	*A.* Rh.	*B.* Rh.	*A.* Pd.	*B.* Pd.	*A.* Ir.	*B.* Ir.
2.....	0·50	0·50	0·53	0·55	0·50	0·39	0·41	0·41	0·28	0·25	0·60	0·58	0·03	0·01	−0·09	0·00	0·01	0·18
4.....	0·52	0·50	0·53	0·55	0·50	0·40	0·42	0·41	0·31	0·27	0·60	0·58	0·04	0·01	−0·07	0·02	0·02	0·19
6.....	0·54	0·50	0·53	0·55	0·49	0·40	0·42	0·41	0·32	0·28	0·61	0·58	0·04	0·01	−0·06	0·03	0·02	0·19
10.....	0·55	0·50	0·53	0·55	0·49	0·40	0·42	0·41	0·33	0·29	0·61	0·58	0·04	0·01	−0·05	0·04	0·03	0·18
20.....	0·56	0·50	0·53	0·55	0·48	0·40	0·42	0·41	0·33	0·30	0·59	0·58	0·03	0·02	−0·04	0·05	0·03	0·18
50.....	0·55	0·50	0·53	0·55	0·46	0·41	0·42	0·41	0·33	0·30	0·58	0·58	0·03	0·02	−0·02	0·06	0·04	0·18
100.....	0·54	0·50	0·54	0·55	0·45	0·42	0·43	0·41	0·32	0·30	0·58	0·57	0·03	0·02	0·00	0·07	0·05	0·17
200.....	0·54	0·50	0·54	0·55	0·45	0·42	0·43	0·42	0·32	0·30	0·58	0·56	0·03	0·02	0·01	0·08	0·05	0·17
400.....	0·53	0·50	0·54	0·54	0·44	0·42	0·43	0·42	0·31	0·29	0·57	0·55	0·03	0·02	0·08	0·08	0·05	0·16
1,000.....	0·50	0·49	0·54	0·54	0·43	0·41	0·44	0·43	0·29	0·29	0·55	0·54	0·03	0·01	0·08	0·05	0·05	0·14
2,000.....	0·48	0·48	0·53	0·53	0·42	0·41	0·44	0·43	0·28	0·28	0·53	0·52	0·01	0·00	0·02	−0·02	0·08	0·12

Cathodic Overvoltages in N*-Sodium Hydroxide.*

Current density.	*A.* Mg.	*B.* Mg.	*A.* Cd.	*B.* Cd.	*A.* Tl.	*B.* Tl.	*A.* Cr.	*B.* Cr.	*A.* Mn.	*B.* Mn.	*A.* Rh.	*B.* Rh.	*A.* Pd.	*B.* Pd.	*A.* Ir.	*B.* Ir.
2	0·56	0·57	0·51	0·55	0·43	0·42	0·46	0·37	0·29	0·27	0·02	0·04	0·25	0·38	0·43	0·46
4	0·57	0·58	0·53	0·60	0·45	0·44	0·46	0·37	0·31	0·29	0·03	0·05	0·27	0·43	0·43	0·54
6	0·58	0·58	0·54	0·62	0·46	0·45	0·46	0·38	0·31	0·29	0·03	0·05	0·28	0·45	0·43	0·59
10	0·59	0·59	0·54	0·64	0·48	0·47	0·45	0·38	0·32	0·30	0·04	0·06	0·31	0·47	0·44	0·62
20	0·61	0·59	0·53	0·65	0·50	0·49	0·45	0·39	0·33	0·31	0·04	0·06	0·32	0·49	0·44	0·64
50	0·64	0·59	0·52	0·66	0·54	0·52	0·44	0·39	0·34	0·32	0·04	0·07	0·34	0·53	0·44	0·65
100	0·67	0·60	0·52	0·66	0·56	0·53	0·42	0·39	0·35	0·33	0·05	0·08	0·36	0·56	0·45	0·65
200	0·67	0·59	0·51	0·67	0·56	0·54	0·42	0·39	0·37	0·34	0·06	0·09	0·36	0·57	0·32	0·65
400	0·68	0·58	0·52	0·67	0·55	0·55	0·41	0·39	0·39	0·35	0·07	0·08	0·36	0·58	0·34	0·64
1,000	0·67	0·58	0·56	0·66	0·54	0·56	0·40	0·39	0·42	0·37	0·08	0·08	0·37	0·58	0·64	0·64
2,000	0·66	0·57	0·61	0·65	0·54	0·55	0·39	0·39	0·45	0·37	0·08	0·07	0·39	0·57	0·63	0·63

obtained in acid, but the reverse is sometimes observed (for example, manganese). Further work on overvoltage in other electrolytes is necessary before these changes can be fully explained. Sodium alloys are formed in the alkali electrolyte with the higher overvoltage metals, especially at high current densities.

Values given in column *B* are generally more typical of the metal than those in column *A*, since the former are the averages of four sets of readings.

The considerations outlined above have led to the construction of the table on p. 1111, reasons for the adoption of individual values being given in the subsequent discussion on the table.

Cathodic Overvoltage of Metals in the Periodic Groups.

In group I the overvoltages of copper, silver, and gold in acid electrolyte show a tendency to attain a normal limit of about 0·35 volt. Copper shows a higher value when first used, but rapidly falls, whilst gold and silver start with lower values but soon rise. Silver shows a lower overvoltage than either copper or gold, and this appears to be typical of metals in series 7 in the first five groups of the table. In alkali, copper is capable of attaining a high overvoltage ($>0{\cdot}6$ volt) when a low current density is applied for a long time. This high value is only found normally in group II, and hence this change of overvoltage is comparable with a change from univalent to bivalent copper. Gold, when treated in the same way, readily acquires an overvoltage of 0·50 volt similar to that of the tervalent metals of group III.

Silver in acid at high current densities has a very low overvoltage (lowest observed, 0·06 volt), suggesting a position in group 0 along with the platinum metals. Similar behaviour is observed with many other metals.

It is probable that the overvoltage of sodium is similar to that of copper, since both metals appear to lower the overvoltage of mercury to the same degree. Mercury in alkali shows a very high overvoltage at first, but this soon falls to about 0·69 volt, and sodium amalgam is formed. Freshly amalgamated copper also shows an overvoltage of 0·69 volt in acid and again in alkali after using for a short time. Such evidence as to the overvoltage of sodium is perhaps unsatisfactory, but no evidence to the contrary has been found.

In group II the highest overvoltages are found. That of magnesium in acid is somewhat difficult to determine owing to the rate at which the metal dissolves. Such measurements as were possible showed the value to be slightly more than 0·70 volt, and experience has shown that the dissolution of a metal with the evolution of

Cathodic Overvoltages in the Periodic System.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
				Carbon.						
2	—	—	—	**0·40** 0·70	—	—	—	—	—	—
	Sodium.	Magnesium.	Aluminium.							
3	**0·34** ?	**0·70**	**0·50** < 0·10	—	—	—	—	—	—	—
						Chromium.	Manganese.	Iron.	Nickel.	Cobalt.
4	—	—	—	—	—	**0·38** 0·42 0·48	**0·30** 0·60	**0·18** 0·25 0·33	**0·18** 0·24 0·30	0·2 0·67
	Copper.	Zinc.								
5	**0·34** 0·60	**0·72**	—	—	—	—	—	—	—	—
						Molybdenum.			Rhodium.	Palladium.
6	—	—	—	—	—	**0·32**	—	—	**0·19** 0·02	0·05 0·34 0·65
	Silver.	Cadmium.		Tin.	Antimony.					
7	**0·30** 0·06	**0·66** 0·50	—	**0·45** 0·66	**0·42** 0·45	—	—	—	—	—
					Tantalum.	Tungsten.	—	—	Iridium.	Platinum.
10	—	—	—	—	**0·41** 0·50	**0·30**			**0·18** 0·04 0·45 0·67	**0·18** 0·06 0·45 0·65
	Gold.	Mercury.	Thallium	Lead.	Bismuth.					
11	**0·32** 0·50	**0·70** 0·00	**0·52**	**0·46** 0·72	**0·43** 0·52	—	—	—	—	—

hydrogen generally has but little effect on the measured cathodic overvoltage. In alkali, the overvoltage of magnesium is almost the same as that of zinc.

The extremely variable nature of the overvoltage of mercury has long been a source of difficulty in accounting for overvoltage. This is probably due in part to its liquid state, which renders the saturation of the surface difficult, if not impossible. Two values of the overvoltage are, however, fairly definite: a very high one, above 0·7 volt, and a very low one approaching zero. The former value is consistent with its position in group II, whilst the latter value would correspond with a position in group 0 along with the inert gases and the platinum metals (see notes on these).

These two values can be maintained under suitable conditions for an indefinite time, whilst intermediate values are rarely constant for more than a few minutes, and are, moreover, liable to sudden violent changes to the very high or very low values.

On one occasion, after a sample of pure mercury had been exposed to a current density of 100 milliamperes per sq. cm. for half an hour, the overvoltage suddenly fell from 0·5 volt to 0·8 volt, and persisted between this value and 0·00 volt until the experiment was stopped half an hour later. On connecting this mercury to a standard mercurous sulphate electrode, a current of 1×10^{-6} ampere was produced for a few seconds only, showing that under these conditions the quantity of hydrogen absorbed by the mercury is extremely small. The same mercury gave a current of 30×10^{-6} ampere falling to 2×10^{-6} ampere in half an hour after its overvoltage had been raised to 0·6 volt.

The overvoltage of cadmium is peculiar. In alkali it rises to 0·67 volt, which is about the value that might be expected from its position in series 7. In acid it acquires a very definite and constant overvoltage of 0·50 volt, thus showing a close resemblance to aluminium and thallium, but salts of tervalent cadmium are unknown. With low current density in acid the overvoltage rises to 0·63 volt, but the value of 0·50 volt still awaits an explanation. So also do the low values, below 0·6 volt, obtained for magnesium and zinc in alkali, although these are probably due to the formation of sodium alloys.

In group III the first metal, aluminium, has marked double values, one of which only appears in acid electrolyte after subjection to a high current density, and is more easily obtained when the surface is highly polished. The higher value is very definite, and varies but little from 0·50 volt in acid or alkali. The lower value approaches zero, but is only stable at very high current density. As the current density is lowered to 10 milliamperes per sq. cm. the

fall in the lower value is counterbalanced by the tendency to revert to the higher values. The low value suggests a position for this element in group 0.

Thallium does not show double values in acid, its overvoltage being remarkably constant at $0{\cdot}53 \pm 0{\cdot}01$ volt. In alkali it is somewhat variable.

In group IV, carbon, tin, and lead have very definite double values, and either set of values is easily produced at will under given conditions.

Gas carbon in acid gives the high values at the higher current densities, whilst graphite gives only the low values at all current densities. In alkali the high values are obtained with both forms.

High values for tin and lead are always produced when the polished metals are used with a low current density. The low values are obtained after the metals have been used as cathodes in acid with a high current density, and when once the low values are produced, the restoration of the high values can only be brought about with difficulty. In alkali, the low values do not appear.

The higher values correspond with those found in group II.

These double values may be compared with the corresponding changes of valency which occur with the three elements.

In group V, antimony, tantalum, and bismuth have overvoltages in acid approaching the typical overvoltage of group III (that is, 0·50 volt) when first used, but this soon falls to 0·42 volt, the typical overvoltage for this group. The values are so close together, especially for antimony, that it appears doubtful if they are really double values or not. Bismuth at very high current densities suddenly acquires a very low overvoltage (lowest observed, 0·05 volt), but the other metals do not show this value.

In alkali, the overvoltages of antimony and bismuth are unexpectedly high, being similar to those of the metals of group II. This behaviour is comparable with that of bismuth salts in the presence of a reducing agent on the addition of alkali hydroxide, when the black oxide, BiO, is formed, in which bismuth appears to be bivalent.

In group VI the overvoltage of chromium in acid is higher than that of molybdenum or tungsten by nearly 0·1 volt. No evidence of double values was obtained in acid, but in alkali, chromium at first shows an overvoltage of 0·48 volt, which falls rapidly to 0·38 volt when the current density is raised above 20 milliamperes per sq. cm., and remains very constant at that value. The former value approaches that of the metals of group III.

The overvoltages of the metals in this group show less variation with time and current density than those of any other group.

Possibly series 4 is one of maximum overvoltages, just as series 7 is one of minimum values. Otherwise it would appear that chromium in acid acts like a quinquevalent metal, since its very constant overvoltage is exactly suited to a position in group V. It has been suggested that the green solution of chrome alum contains a salt of chromosulphuric acid, $HCr(SO_4)_2$, in which chromium has this valency.

In group VII the only metal manganese shows very marked double values.

In acid electrolyte where the tendency to form salts of the bivalent metal is marked, the high overvoltage characteristic of metals of group II is obtained.

In alkali the tendency to form salts of manganic and permanganic acid is much greater, and the overvoltage is intermediate between that of chromium in group VI and iron in group VIII.

The sample of metal used contained iron, carbon, silicon, and phosphorus, and probably not more than 97 per cent. of manganese. Hence the values given may be several per cent. in error. The metal was acted on slowly with evolution of hydrogen in the acid electrolyte.

Group VIII shows an extremely complicated series of overvoltages, and it is a difficult matter to determine the normal value. Two series of values are repeatedly observed approaching 0·18 volt and 0·25 volt respectively, and these both appear to be characteristic of this group. All the metals in the group, with the exception of rhodium and palladium, readily give one or both of these values, whilst other values are only obtained under special conditions.

Iron and nickel show both values and also higher values of about 0·32 volt corresponding with that found in group VI. Cobalt shows the second of the above values fairly consistently, but also acquires the high overvoltage characteristic of group II after subjection to a high current density in alkali. All the platinum metals show overvoltages approaching zero, specially when coated with the same metal in the 'black' condition. Rhodium keeps this low overvoltage under very varied conditions, but a value of 0·19 volt was attained after three hours in alkali with a current density of 100 milliamperes per sq. cm. Palladium also keeps the low values in acid if the current density is maintained fairly high, but with low current density the overvoltage rapidly rises to high, but variable, values, in the neighbourhood of 0·45 volt. It is difficult for long periods to prevent the overvoltages of platinum and iridium in acid from rising to 0·18 volt, and at low or moderate current densities values of 0·45 volt or a little higher are attained in a few hours,

remaining fairly constant at this stage. Platinised platinum under similar conditions acquires an overvoltage of 0·25 volt. In alkali the three metals palladium, iridium, and platinum do not show the very low values, and readily acquire the high overvoltages of the group II metals when subjected to moderate current densities, values slightly below 0·7 volt being obtained in each case. Iridium when first used in alkali shows a very constant overvoltage of 0·44 volt corresponding with that in group IV. When the current density is increased from 100 to 200 milliamperes per sq. cm., a sudden rise to the high values of group II occurs. As the current density is reduced, the high value persists until quite low current density is applied, when a rapid fall takes place to the previous values. Iridium thus shows four very definite values, 0·0 volt and 0·18 volt in acid, and 0·44 volt and 0·67 volt in alkali. Between these values the change of overvoltage is rapid. The behaviour of palladium and platinum is similar.

The two values 0·18 volt and 0·25 volt found in this group may perhaps be better explained in the following way.

The overvoltage of chromium is at least 0·05 volt higher than that of molybdenum or tungsten; hence the lower value for manganese, 0·30 volt, may be higher than the typical overvoltage for group VII by 0·05 volt. This would mean that the values near 0·25 volt found for iron, nickel, cobalt, palladium, and platinum under certain conditions are really representative of group VII, an arrangement which gives a much greater degree of symmetry to this part of the table.

The following table shows the distribution of the metals in the groups, those which have the overvoltage of a group to which they do not properly belong being placed in brackets.

Cathodic Overvoltages of the Periodic Groups.

Group 0.—Typical overvoltage, 0·0 volt; (silver), (mercury), (aluminium), (bismuth), (nickel), (rhodium), (palladium), (iridium), (platinum).

Group I.—Typical overvoltage, 0·35 volt; sodium, copper, silver, gold.

Group II.—Typical overvoltage, 0·70 volt; magnesium, zinc, cadmium, mercury, (carbon), (tin), (lead), (antimony), (bismuth), (manganese), (cobalt), (palladium), (iridium), (platinum).

Group III.—Typical overvoltage, 0·50 volt; aluminium, thallium, (antimony), (tantalum), (bismuth).

Group IV.—Typical overvoltage, 0·45 volt; carbon, tin, lead, (iridium), (platinum).

Group V.—Typical overvoltage, 0·42 volt; antimony, tantalum, bismuth, (chromium).

Group VI.—Typical overvoltage. 0·32 volt; chromium, molybdenum tungsten, (iron), (nickel).

Group VII.—Typical overvoltage, 0·25 volt; manganese, (iron), (nickel), (cobalt), (palladium), (platinum).

Group VIII.—Typical overvoltage, 0·18 volt; iron, nickel, rhodium, iridium, platinum.

The only metals in this table which do not appear in their proper groups are cobalt and palladium. Values for cobalt as low as 0·18 volt have not been obtained. Palladium shows values above and below the group value, but in the neighbourhood of the group value the overvoltage is indefinite and changing rapidly.

Reviewing the table as a whole, a rise of overvoltage of two equal steps is observed from group 0 to group II, followed by a gradual fall through the rest of the table.

Where metals have overvoltages corresponding with more than one group, compounds of these metals are known in nearly all cases in which the metal shows a valency corresponding with that of the other metals of the groups with which it is placed.

In conclusion, it may be pointed out that although many of the cathodic overvoltages given in the table may appear to have been chosen somewhat arbitrarily, yet the regularities observed are much too pronounced to be completely dependent on such arbitrary choice. Equally good, and in some respects better, regularity may be observed by taking the maximum or minimum overvoltages for each metal instead of the average values as given, but if this is done, the decision as to the maximum or minimum for each member of a set of values for the same electrode becomes more difficult.

Cathodic overvoltage must therefore be considered as one of the definite periodic properties of the elements.

Anodic Overvoltages and the Periodic Law.

The anodic overvoltages of metals in the periodic groups do not show the same degree of regularity as the cathodic. There are two main reasons for this:

(1) It is impossible to obtain an aqueous electrolyte having only one anion while any dilute acid gives a single cation. In the dilute acid used for these experiments, the four anions, O'', OH', HSO_4', and SO_4'', are present, whilst in the alkaline electrolyte O'' and OH' are present. Hence it is very difficult to decide on the standard potential from which to calculate anodic overvoltage. Hydrogen dissolves in palladium, platinum, etc., in the monatomic state, and therefore it is quite possible that hydroxyl occurs as such on or within the anode surface. The standard electrode for comparison in such cases would not be an oxygen electrode, but one surrounded with a mixture of oxygen and hydroxyl in the correct proportions.

(2) In most cases, fairly stable oxides or peroxides are formed, and some of these are poor electrical conductors. A partly insulating film will then cover the electrode surface, forming the dielectric of a condenser which is charged by the applied electromotive force and then discharged through the potentiometer, giving abnormally high values for the anodic overvoltage. This behaviour is shown by antimony, bismuth, tungsten, etc.

The first of these two reasons is probably responsible for the fact that overvoltages calculated from an oxygen electrode as standard are abnormally high compared with cathodic overvoltages.

Caspari, using an indefinitely low current density, obtained a value for the anodic overvoltage of platinum about 0·3 volt lower than the average of those given in these tables. Under the experimental conditions of Caspari's work, the oxygen ions present were probably sufficient to carry the small current used, whilst in the present work other ions certainly took part.

If the anodic overvoltages are recalculated on the assumption that the potential of the normal standard is 0·3 volt above that of an oxygen electrode, we obtain a series of values which in many cases show a considerable resemblance to cathodic overvoltages of the same metal. The parallelism is, however, very rough, and in many cases an anodic overvoltage measured in alkali only corresponds with a cathodic overvoltage found in acid.

A few of the best examples are given below, where column I shows the average anodic overvoltage, generally in alkali, and column II the corresponding cathodic overvoltage.

Metal.	I. Anodic. Volt.	II. Cathodic. Volt.
Copper	0·32	0·34
Silver	0·41	0·43
Zinc	0·63	0·60
Lead	0·64	0·67
Nickel	0·27	0·24
Cobalt	0·25	0·28
Palladium	0·35	0·34
Iridium	0·18	0·18
Platinum	0·60	0·65
Manganese	0·62	0·60

It may be noted here that the anodic overvoltage of lead covered with peroxide corresponds with the cathodic overvoltage of a bivalent metal. According to Liebenou's theory of the lead accumulator, lead peroxide ionises directly, giving a PbO_2'' ion and forming plumbites in which the lead is definitely bivalent.

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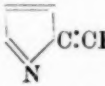
[*Received, October 3rd,* 1916.]

LXXX.—*The Condensation of Pyrrole-2-aldehyde with Ketones.*

By Eva Lubrzynska.

It has been stated by Angeli and Marchetti (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 360) that since pyrrole-2-aldehyde does not react with dihydroxyammonia, $NH(OH)_2$, and does not give the corresponding hydroxamic acid, $RC(NOH)\cdot OH$, this substance probably does not exist in the aldehydic form, but is represented by the hydroxymethylenic formula,

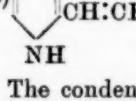
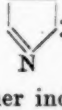


Alessandri (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 194), who isolated the sodium salt of pyrrole-2-aldehyde, appears to hold the same view. On the other hand, the fact that the hydrogen sulphite compound, the *p*-nitrophenylhydrazone and oxime (Bamberger and Djerdjian, *Ber.*, 1900, **33**, 536), as well as the semicarbazone (Tschelincev and Terentjev, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1405), of this substance have been obtained, shows that it can also react in its aldehydic form.

Since comparatively little is known about pyrrole-2-aldehyde, and since it seems to possess some peculiar properties, it was interesting to investigate whether it was capable of giving the usual reactions of condensation characteristic of aldehydes.

I undertook, therefore, to study the condensations of this aldehyde with ketones possessing the grouping $CH_3\cdot CO\cdot$, the reaction being carried out in weak alkaline solution.

The reactions of pyrrole-2-aldehyde with acetone, methyl ethyl ketone, and acetophenone were investigated. In all these cases there were obtained yellow, crystalline products of the type: 1 molecule aldehyde + 1 molecule ketone $- H_2O$, to which the following structure can be given:

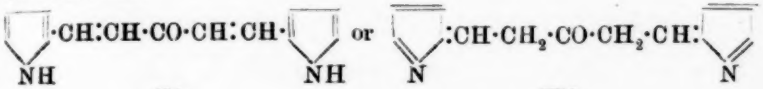
(*a*)  or its tautomeric form:  .

The condensation takes place in the manner indicated, since the pyrrole ring itself is known to condense with acetone only in the presence of acids (Tschelincev and Tronov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 120), and since no instances of condensation of pyrrole rings with ketones in the presence of alkalis are known.

In the case of the condensation of pyrrole-2-aldehyde with

acetone in addition to the yellow, crystalline product of the type usually obtained (melting at 112—113°), a very small quantity of another substance (only 0·03 gram) of an intense orange colour was obtained on one occasion, which at 90° becomes yellow and melts at 185—186°.

Since the yellow substance (m. p. 112—113°) in alkaline solution and in the presence of pyrrole-2-aldehyde was observed to change partly into the orange variety, it is possible that this orange condensation product of pyrrole-2-aldehyde with acetone may have the constitution:



(I.) (II.)

but up to the present such small quantities of this orange condensation product (m. p. 185°) have been obtained that it has not yet been possible to analyse and define it. The investigation of this substance is being continued.

Experimental.

*Condensation of Pyrrole-2-aldehyde with Acetone.**

Pyrrole-2-aldehyde (2·8 grams) was dissolved in 100 c.c. of water and 6 c.c. of pure acetone, together with 6 c.c. of *N*-potassium hydroxide, were added to the solution. The mixture was warmed on a water-bath for ten minutes, and on the following day about 3 grams of a yellow, crystalline compound were obtained, which after several recrystallisations from benzene melted at 112—113°. The product obtained in this way consisted of slender, yellow needles attaining 1 cm. in length; they dissolve readily in hot benzene or light petroleum, and are sparingly soluble in ether or cold water. The substance gives an intense red coloration with hydrochloric acid, but no coloration with a solution of ferric chloride.

Found: C = 71·20; H = 6·81:

0·1257 gave 11·55 c.c. N_2 at 15·25° and 745 mm. N = 10·55.

0·0517, in 15·3 benzene, gave $\Delta^t = -0·109°$. M.W. = 155.

C_8H_9ON requires C = 71·07; H = 6·71; N = 10·37 per cent.

M.W. = 135.

Condensation of Pyrrole-2-aldehyde with Methyl Ethyl Ketone.

This condensation was carried out in a manner similar to that described above. Pyrrole-2-aldehyde (2·1 grams) was dissolved in

* This part of the work was carried out in the Organic Chemistry Laboratories of Moscow University, and I wish to express my gratitude to Professor W. W. Tschelincev for his kind help and advice.

75 c.c. of water, and to this solution were added 7 c.c. of *N*-potassium hydroxide and 12 c.c. of the ketone. The mixture was warmed on a water-bath for a short time, and the following day a yellow, crystalline precipitate was obtained. The condensation product was recrystallised several times from light petroleum, when pale yellow needles melting at 98—99° were obtained.

Found: C=72·58; H=7·58:

0·1033 gave 8·7 c.c. N_2 at 18° and 753 mm. N=9·61.

$C_9H_{11}ON$ requires C=72·49; H=7·43; N=9·40 per cent.

Condensation of Pyrrole-2-aldehyde with Acetophenone.

Pyrrole-2-aldehyde (0·9 gram) was dissolved in water to which a little alcohol had been added, then 3 c.c. of pure acetophenone and 3 c.c. of *N*-potassium hydroxide were poured into the solution. The whole was warmed on a water-bath for ten minutes. A few days later the solution became yellow and cloudy, and a fine, yellow precipitate began to be formed. Four weeks later the precipitate was crystallised twice from alcohol, when it melted at 138—139°.

Found: C=79·31; H=5·68:

0·1434 gave 9 c.c. N_2 at 14° and 751 mm. N=7·25.

$C_{13}H_{11}ON$ requires C=79·15; H=5·63; N=7·11 per cent.

PETROGRAD. [*Received, September 4th*, 1916.]

LXXXI.—*The Constitution of Carbamides. Part III. The Reaction of Urea and of Thiourea with Acetic Anhydride. Note on Potassium Thiourea.*

By EMIL ALPHONSE WERNER.

WHILST it is well known that acetylurea and acetylthiourea can be obtained by heating the respective parent compounds with acetic anhydride, no quantitative study of these interactions has hitherto been recorded, nor has any particular attention been given to the secondary changes which accompany the formation of the acetyl derivatives. A study of these changes has brought to light some facts of interest that support the cyclic formulæ of urea and of thiourea which have been put forward by the author (T., 1912, **101**, 2185; 1913, **103**, 1014, 2281; 1914, **105**, 924; 1915, **107**, 715).

Urea and Acetic Anhydride.

When urea is heated with acetic anhydride, carbon dioxide is freely evolved as soon as the boiling point (138°) is reached, and the greater part of the urea is decomposed with the production of acetamide and diacetamide.

The dissociation of urea and the rapid interaction of the products, ammonia and cyanic acid (in the keto-form) and acetic anhydride, are responsible for the velocity of this decomposition, which from a quantitative point of view must be considered as the primary change, and is represented by the following equations:

(*a*) $HN{:}C\langle\begin{matrix}NH_2\\|\\O\end{matrix} + (CH_3{\cdot}CO)_2O =$

$$CH_3{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}CO_2H + HN{:}CO.$$

(*b*) $HN{:}CO + (CH_3{\cdot}CO)_2O = (CH_3{\cdot}CO)_2NH + CO_2.$

In consequence, the yield of acetylurea from direct acetylation is poor. Thus when urea was heated under reflux with acetic anhydride for different intervals of time, the yields of acetylurea, calculated in percentages of the theoretical, were as follows:

TABLE I.

	Time in minutes.	Acetylurea formed. Per cent.
Expt. 1	2·5	21·6
„ 2	5·0	34·9
„ 3	10·0	34·8
„ 4	15·0	27·3
„ 5	20·0	23·9

Whilst the maximum yield of acetylurea was obtained after five to ten minutes' heating, the rest of the urea was found to have been completely decomposed in accordance with equations (*a*) and (*b*). The results show conclusively that direct acetylation and the main decomposition proceed simultaneously from the outset of the interaction.

These facts are in agreement with the view already put forward (T., 1913, *loc. cit.*) that when urea is heated to a temperature above its melting point in a solvent, such as acetic anhydride, dissociation of urea molecules is accompanied by a certain amount of change to the form $HN{:}C\langle\begin{matrix}NH_2\\OH\end{matrix}$. It is the latter form of the molecule that is acetylated.

When the cyclic configuration of the urea molecule was changed to this form by the addition of a sufficiently strong acid, the decomposition represented by equations (*a*) and (*b*) was almost entirely suppressed, and the yield of acetylurea was largely increased.

Thus when urea was heated with acetic anhydride in presence of a small quantity of sulphuric acid, the yield of acetylurea was nearly 80 per cent. of the theoretical, and in spite of a rather violent reaction very little carbon dioxide was evolved. Acetylurea was found to separate unchanged from its solution in warm acetic anhydride, but when further heated with the reagent it was gradually decomposed with the formation of the products shown in (*a*) and (*b*); to this cause was due the fall in the yield of acetylurea after ten minutes' heating, shown in the results above.

No further acetylation of urea could be detected in these experiments. It was in an unsuccessful attempt to obtain diacetylurea in this way that Hofmann (*Ber.*, 1881, **14**, 2733) first showed that diacetamide and acetamide were produced when urea was heated with acetic anhydride.

Quite recently, Kohmann (*J. Amer. Chem. Soc.*, 1915, **37**, 2131) has shown that no diacetylurea could be obtained in this way. Now, according to the author's views, the further acetylation of acetylurea should give rise to the formation of a diacetylurea, derived from the so-called "*iso*carbamide" configuration, which should have the constitution $HN{:}C\!<\!\begin{matrix}NH\cdot CO\cdot CH_3\\O\cdot CO\cdot CH_3\end{matrix}$. Such a diacetyl derivative has been quite readily obtained by the action of acetic anhydride on acetylurea at 60° in the presence of a small quantity of sulphuric acid; the yield was quantitative, in accordance with the equation:

$$HN{:}C\!<\!\begin{matrix}NH\cdot CO\cdot CH_3\\OH\end{matrix} + (CH_3\cdot CO)_2 = HN{:}C\!<\!\begin{matrix}NH\cdot CO\cdot CH_3\\O\cdot CO\cdot CH_3\end{matrix} + CH_3\cdot CO_2H.$$

The compound forms slender, snow-white needles melting at 153·5°, which are sparingly soluble in cold water or alcohol.

Evidence in support of the above constitution was afforded by the fact that an acetyl group was completely removed by gently warming the compound with aqueous sodium hydroxide for a few minutes, whilst water alone at 100° hydrolysed the compound fairly rapidly, according to the equation:

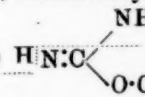
$$HN{:}C\!<\!\begin{matrix}NH\cdot CO\cdot CH_3\\O\cdot CO\cdot CH_3\end{matrix} + H_2O = HN{:}C\!<\!\begin{matrix}NH\cdot CO\cdot CH_3\\OH\end{matrix} + CH_3\cdot CO_2H,$$

Thus, in an *N*/4-solution, 21 per cent. was hydrolysed after one hour.

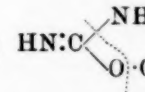
Acetylurea, on the other hand, is very stable in water at 100°. Diacetylurea commences to decompose at 170°; the chief products of decomposition were acetamide, acetonitrile, and carbon dioxide,

whilst small amounts of diacetamide and of cyanuric acid were also formed.

These results indicate a cleavage of the molecules in two directions, which may be represented as follows:

(1)  =

$$CH_3\cdot CO\cdot NH_2 + CH_3\cdot CO\cdot O\cdot CN \longrightarrow CH_3\cdot CN + CO_2.$$

(2)  $= HN(CO\cdot CH_3)_2 + HNCO$ (polymerised).

Considering the properties of diacetylurea, it was not surprising that it has not been found possible to prepare the compound by the direct acetylation of urea in a single operation; the heat developed in the first stage establishes a condition which precludes such a possibility.

The compound is identical with the diacetylurea (m. p. 153°) first obtained in small quantity by Schmidt (*J. pr. Chem.*, 1872, [ii], **5**, 63) from the products of the interaction of carbonyl chloride and acetamide at 50°, which has been assumed, without any experimental evidence, to have the constitution $CO(NH\cdot CO\cdot CH_3)_2$.

Thiourea and Acetic Anhydride.

When thiourea was heated with acetic anhydride, the main change was direct acetylation with the production of a mixture of the monoacetyl and diacetyl derivatives; decomposition, with evolution of carbonyl sulphide, corresponding with equations (*a*) and (*b*), as in the case of urea, took place only to a very small extent, unless the heating was prolonged, when the acetyl derivatives were gradually decomposed.

As regards the production of diacetylthiourea, Kohmann (*loc. cit.*) has forestalled the author in describing the isolation of the compound for the first time.

The chief interest connected with the preparation of this compound, which, as a matter of fact, the author had isolated more than three years ago, lies in the question of its constitution and in the explanation of the conditions which promote its formation. Neither of these points was investigated by Kohmann, who has been misled in assuming that the compound must be represented by the constitutional formula, $CS(NH\cdot CO\cdot CH_3)_2$.

Like its urea analogue, this compound is derived from the "*iso*thiourea" configuration, and has the constitution,

$$HN{:}C\begin{cases} NH\cdot CO\cdot CH_3 \\ S\cdot CO\cdot CH_3 \end{cases}.$$

It has been obtained in a yield amounting to more than 75 per cent. of the theoretical by heating thiourea with acetic anhydride in the presence of hydrogen chloride. The pure compound forms bright lemon-yellow prisms, which melt at 153° (Kohmann gives 151—152°).

The aqueous solution was easily desulphurised in the cold on addition of an alkaline lead solution.

Diacetylthiourea was rapidly hydrolysed when heated in aqueous solution; thus, in an $N/4$-solution at 100°, 40 per cent. was hydrolysed after thirty minutes, and 93 per cent. after one hour; as might be expected, it is much less stable in this respect than the urea analogue. Whilst the main change was the loss of the acetyl group previously in union with sulphur, in accordance with the equation:

(*c*) $HN{:}C\begin{matrix}NH\cdot CO\cdot CH_3\\ S\cdot CO\cdot CH_3\end{matrix} + H_2O =$

$$HN{:}C\begin{matrix}NH\cdot CO\cdot CH_3\\ SH\end{matrix} + CH_3\cdot CO_2H,$$

a certain amount of the compound was decomposed in the following manner:

(*d*) $HN{:}C\begin{matrix}NH\cdot CO\cdot CH_3\\ S\cdot CO\cdot CH_3\end{matrix} + H_2O =$

$$CH_3\cdot CO\cdot SH + CH_3\cdot CO_2H + CN\cdot NH_2.$$

The latter change was more marked in the presence of a strong acid. Monoacetylthiourea was scarcely affected after heating its aqueous solution for one hour at 100°.

Advantage has been taken of the rapid hydrolysis of diacetylthiourea in order to estimate the proportion of the two acetyl derivatives produced when thiourea was heated with acetic anhydride for different intervals of time.

The following results, expressed in percentages of the theoretical yields, were obtained:

TABLE II.

CSN_2H_4 and $(CH_3\cdot CO)_2O$. Ratio, 1:2 molecular proportions. $t = 138°$.

	Time in minutes.	Acetylthiourea. Per cent.	Diacetylthiourea. Per cent.	Combined products. Per cent.
Expt. 6	2·5	46·9	42·3	89·2
„ 7	5·0	42·3	46·7	89·0
„ 8	10·0	37·3	50·0	87·3
„ 9	15·0	37·7	48·4	86·1

TABLE III.

CSN_2H_4 and $(CH_3\cdot CO)_2O$. Ratio, 1:1·5 molecular proportions. $t=138°$.

	Time in minutes.	Acetylthiourea. Per cent.	Diacetylthiourea. Per cent.	Combined products. Per cent.
Expt. 10 ...	2·5	46·6	28·5	75·1
„ 11 ...	5·0	49·5	31·1	80·6
„ 12 ...	10·0	55·9	27·4	83·3
„ 13 ...	15·0	58·6	23·7	82·3

It has not been found possible to effect a satisfactory quantitative separation of the acetyl compounds by the aid of any solvent, but in so far as the best conditions for the preparation of acetylthiourea were concerned, these have been brought to light by the results of the above experiments. Thus, when the product of Expt. 8, where the largest yield of diacetylthiourea is shown, was boiled with water for seventy minutes, a yield of pure acetylthiourea (m. p. 168°) equal to more than 82 per cent. of the theoretical, was obtained.

Before considering the information of theoretical interest supplied by the above results, it was necessary to confirm the constitution of acetylthiourea, since it has been suggested by Prätorius (*J. pr. Chem.*, 1880, [ii], **21**, 147) that this derivative should be represented by the formula $HN{:}C\langle^{NH_2}_{S\cdot CO\cdot CH_2}$.

The stability of the compound, the formation of acetylcyanamide in quantitative yield on addition of ammonio-silver nitrate in the cold, and again the production of acetamide and thiocyanic acid (with its decomposition products) prove conclusively that the acetyl group is in union with nitrogen.

In further proof of the constitution of diacetylthiourea, this compound, when decomposed by heat, gave as chief products acetamide and acetyl thiocyanate,* thus:

(*e*) $HN{:}C\langle^{NH\cdot CO\cdot CH_3}_{S\cdot CO\cdot CH_3}$ =

$$CH_3\cdot CO\cdot NH_2 + CH_3\cdot CO\cdot SCN \rightleftharpoons CH_3\cdot CO\cdot NCS.$$

According to the author's views, the properties of acetylthiourea may be best represented as the result of a condition of equilibrium between two molecular forms, thus:

$$HN{:}C\langle^{NH_2\cdot CO\cdot CH_3}_{S} \rightleftharpoons HN{:}C\langle^{NH\cdot CO\cdot CH_3}_{SH}.$$

α. β.

* This compound has been shown by Dixon (T., 1905, **87**, 468) to be a mixture of thiocyanate and *iso*thiocyanate.

the change from α to β being promoted in solution by heat, or by the presence of either an acid or a base. Diacetylthiourea would be derived from the attack of acetic anhydride on the β-form.

The almost complete absence in the early stages of the interaction of thiourea and acetic anhydride of any change corresponding with equations (*a*) and (*b*) in the case of urea is explained by the fact that thiourea is not dissociated in solution below 140°; hence, when the proportion of acetic anhydride was favourable, both acetyl derivatives were very rapidly produced (Expts. 6 and 7, table II), and in nearly equal proportions of the theoretical.

It will be noticed that the maximum yield of diacetylthiourea was only half of the theoretical (Expt. 8); this was due to decomposition according to equation (*e*), the progress of which was more rapid, as the heating was prolonged, than the change of acetylthiourea to the β-form suitable for further attack by the acid anhydride. When the latter change was promoted by the addition of hydrochloric or sulphuric acid in agreement with theory, the yield of diacetylthiourea was raised to nearly 80 per cent. of the theoretical amount.

As regards the results in table III, since the proportion of acetic anhydride was not favourable for the production of diacetylthiourea, the quantities formed were naturally much lower, but they show that from the outset of the interaction a condition suitable for further acetylation must obtain, which is in agreement with the view of the constitution of acetylthiourea already stated. It may be mentioned that the highest proportion of the monoacetyl derivative formed in a single operation is shown in the results of Expt. 13.

Potassium Derivative of Thiourea.

A considerable number of additive compounds of thiourea with various metallic salts are known, but no metallic derivative of thiourea has been hitherto described.

Whilst the salts of thiourea have undoubtedly the constitution $HN{:}C\begin{matrix}NH_2\cdot HX\\SH\end{matrix}$, a metallic derivative would be represented by the formula $HN{:}C\begin{matrix}NH_2\\SM\end{matrix}$.

The compound, $CSN_2H_3K(CSN_2H_4)_2$, was easily obtained when thiourea was gently heated with potassium ethoxide or potassium hydroxide in the presence of alcohol. It crystallised from solution in felted masses of delicate needles with a satiny lustre which melted at 145°.

Attempts to obtain the compound CSN_2H_3K in crystalline form free from combined thiourea have not been successful on account

of the readiness with which the potassium derivative was decomposed in solution.

On the other hand, evidence of its constitution and of the completion of the interaction, $CSN_2H_4 + KOH = CSN_2H_3K + H_2O$, was obtained by treating the residue, after heating to 120° in a current of dry hydrogen to remove all solvent, with acetic anhydride, when a large yield of diacetylthiourea was obtained.

Potassium thiourea commenced to decompose at about 160° with evolution of ammonia; the other products were potassium thiocyanate, potassium hydrosulphide, and melamine (from the polymerisation of cyanamide). These results prove that the compound has the constitution $HN{:}C{<}^{NH_2}_{SK}$.

Experimental.

The following method was adopted in estimating the amount of acetylurea formed when urea was heated with acetic anhydride alone for different intervals of time.

Six grams of urea and 15 grams of acetic anhydride were heated under reflux to the boiling point (138°), 30 c.c. of cold water were added, and the product was allowed to remain for eighteen hours. The acetylurea which separated was collected, dried at 100°, and weighed. The solubility of acetylurea in water at 15° was found to be 2·02 per cent.; hence, 0·606 gram was added in each case to the weight obtained as a correction for the amount held in solution.

The theoretical yield of acetylurea is 10·2 grams from 6 grams of urea; from the weights obtained, the results given in table I were calculated.

Preparation of Acetylurea.

A very considerable increase in the yield was obtained in the following manner: 30 grams of urea, 70 grams of acetic anhydride, and 20 grams of pure acetic acid to which 1·5 c.c. of sulphuric acid had been added were carefully heated until a fairly violent reaction started, which was checked by immersion of the flask in cold water. One hundred grams of water were added, and after a few hours the acetylurea which had separated was collected, dried, and weighed; 39·88 grams were obtained, equal to 78·2 per cent. of the theoretical. Thus, the yield was more than doubled by this modification, which is of some practical interest, since acetylurea has been used, through its bromo-derivative, in the preparation of certain "synthetic" drugs.

Preparation of Diacetylurea.

Five grams of acetylurea were heated to 60° with 10 grams of acetic anhydride and 1 c.c. of sulphuric acid was added, when almost at once the acetylurea dissolved and there was slight development of heat. On cooling, the product set to a mass of minute, slender, silky needles, which were collected and washed with ether and alcohol and proved to be pure diacetylurea. The yield, which was 7·2 grams, was quantitative. (Found, N = 19·51. $C_5H_8O_3N_2$ requires N = 19·44 per cent.)

Diacetylurea may be recrystallised from solution in 50 per cent. acetic acid without sensible decomposition.

Action of Heat.—The compound (7·2 grams) was heated in a short tube immersed in a glycerol-bath, which carried a thermometer and was connected with a small condenser.

The compound melted at 153·5°, at 170—180° carbon dioxide was slowly evolved, and the liquid became yellow and opalescent; at 190° a flocculent, yellow precipitate appeared, and the temperature was raised to 200° and maintained for thirty minutes. During this period, 1 gram of a colourless liquid had distilled, which proved to be acetonitrile (b. p. 82°). The residue, which had a strong odour of acetamide, was treated with water, when 0·4 gram of an orange-yellow powder separated; by concentration of the filtrate, 0·29 gram of a micro-crystalline powder was obtained, which was cyanuric acid, and amounted to 4·02 per cent. of the weight of diacetylurea taken. The crystalline residue obtained from further evaporation, after drying, weighed 2·9 grams (40·2 per cent. of the original weight taken), and was nearly pure acetamide. The orange-yellow powder would appear to be a polymerised product from acetylcyanate which had escaped decomposition, thus: $CH_3{\cdot}CO{\cdot}OCN = CH_3{\cdot}CN + CO_2$. It was insoluble in all the usual solvents, and when strongly heated charred and evolved a pungent odour; it contained nitrogen.

The foregoing results are expressed by the equations (1) and (2) already given.

Preparation of Diacetylthiourea.

Fifteen grams of thiourea were heated with 45 grams of acetic anhydride until dissolution was just complete; hydrogen chloride, from 5 grams of sodium chloride, was passed into the liquid whilst the temperature was raised to 130°. The solution, which had assumed a reddish-brown colour, was allowed to cool, and the semi-solid mass was collected, washed with ether, and dried. The yield was 25 grams, or 78·1 per cent. of the theoretical. An equally good

yield was obtained by the addition of 1 gram of sulphuric acid in place of the hydrochloric acid.

Diacetylthiourea was easily obtained in a pure state, and with very little loss, by crystallisation from its solution in 50 per cent. acetic acid, provided the temperature was not raised beyond 70°; the addition of animal charcoal readily removed the red colouring matter. (Found, S = 20·4; N = 17·61. $C_5H_8O_2N_2S$ requires S = 20; N = 17·5 per cent.)

In order to estimate the proportions of the two acetyl derivatives formed when thiourea was heated with acetic anhydride alone, the first stage in the process was carried out as in the experiments with urea. Having obtained the weight of the combined products, 1·6 grams of the well-powdered material were boiled with 40 c.c. of water under reflux for seventy minutes, after which the cold solution was titrated with *N*-sodium hydroxide (using phenolphthalein as indicator). Since 1·6 grams of pure diacetylthiourea (M.W. = 160) after such treatment were found to neutralise 10 c.c. of the alkali, the percentage of diacetyl derivative present in a mixture of the two was directly obtained as a result of the titration. From this the relative proportions with reference to the theoretical yields were easily calculated (tables II and III).

The solubility of acetylthiourea in water at 15° was found to be 1·28 per cent.; hence, 0·384 gram was added in each case to the weight obtained; diacetylthiourea is very sparingly soluble in cold water.

Action of Heat on Acetylthiourea.

Ten grams were heated in a tube, immersed in a glycerol-bath, at 190—195°, when decomposition set in with brisk evolution of carbon disulphide. After the heating had been maintained for thirty minutes at this temperature, the residue was treated with water, when 0·35 gram of a pale brown, amorphous powder separated. The filtrate, on evaporation and distillation, gave 4·2 grams of acetamide, whilst theory requires 5 grams, from the equation $HN{:}C\langle^{NH\cdot CO\cdot CH_3}_{SH} = CH_3\cdot CO\cdot NH_2 + HSCN$. The carbon disulphide (1·4 grams), when shaken with water, gave a strongly acid solution, which produced on addition of ferric chloride a deep, blood-red colour due to thiocyanic acid, much of which had been decomposed, thus: $2HSCN = CS_2 + CN_2H_2$. The amorphous substance was identified as thioammeline; it gave a picrate (decomposed at 230°) identical with that obtained from a specimen of thioammeline, synthesised from the interaction of cyanamide and thiocyanic acid solution, thus:

$$2CN_2H_2 + HSCN = HN\langle^{CS\text{——}NH}_{C(:NH)\cdot NH}\rangle C{:}NH.$$

Nearly half a gram of dicyanodiamide was also obtained from the residue before distillation of the acetamide.

Desulphurisation of Acetylthiourea.

To 2·95 grams of acetylthiourea dissolved in 100 c.c. of water at 60°, 8·5 grams of silver nitrate in solution as the ammonio-salt were added. The filtrate, from the precipitate of silver sulphide which was immediately formed, was evaporated at 100°; from the residue acetylcyanamide in quantitative yield was obtained by extraction with ether. The silver salt was prepared by precipitation with ammonio-silver nitrate:

0·103, dissolved in dilute HNO_3, required 5·4 c.c. $N/10$-KSCN. Ag = 56·62.

$C_3H_3ON_2Ag$ requires Ag = 56·54 per cent.

Acetylcyanamide was found to be quite stable at 100°.

Analyses of the Potassium Derivative of Thiourea.—The compound was instantly decomposed when dissolved in water:

0·1928 required for neutralisation 7·4 c.c. $N/10$-HCl. K = 14·96.
0·0596 „ 6·6 c.c. $N/10$-iodine. CH_4N_2S = 85·26.
$(CH_4N_2S)_2,CH_3N_2SK$ requires K = 14·66. CH_4N_2S = 85·71 per cent.

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TRINITY COLLEGE, DUBLIN: [*Received, September 22nd*, 1916.]

LXXXII.—*The "Cyclic Theory" of the Constitution of Complex Inorganic Compounds: A Criticism.*

By EUSTACE EBENEZER TURNER.

FRIEND, in 1908 (T., **93**, 260, 1006), put forward what he called an electrochemical theory of valency. He assumed that every element possesses one or more of three kinds of valency—free positive, free negative, and latent valency. From his discussions one concludes that all elements, including the Ramsay gases, possess latent valency of some kind, which, however, one cannot distinguish from the vague force which is supposed to exist between the constituent molecules in a "molecular compound." Thus, by means of latent valency, oxygen, normally bivalent, forms oxonium compounds. In this respect the theory seems valuable, since apparently any type of "per" compound can be explained; and although the

theory is inexplicit, we may esteem it in that it avoids unpleasant exceptions.

One or two points, however, seem to be somewhat obscure. Friend assumes that in ammonia the three negative valencies of nitrogen are saturated, and that "a fourth cannot be called out unless it is accompanied by an equal positive valency." In an amine-oxide, therefore, the three negative valencies of the nitrogen atom are satisfied by the three alkyl groups, the oxygen atom being attached by two latent valencies from the nitrogen, one negative and the other positive. Since Friend postulates that oxygen has free negative valency only (for obviously we cannot stretch the point and refer the matter to the latent valency of the oxygen), we have here an example of two negative valencies saturating each other, which is contrary to his usual assumptions.

A similar difficulty seems to occur in connexion with the structure (if such a term is allowable) of nitrogen peroxide. Friend explains how an unsaturated NO molecule passes into N_2O_4, but he does not suggest a formula for NO_2. Oxygen having two free negative valencies and nitrogen having three positive valencies, we see that one and a half oxygen atoms are able to find partners among the nitrogen valencies, the last half atom of oxygen, however, remaining unsaturated. Here, again, one can scarcely "call out" latent valencies. If one does, one comes to the conclusion that nitrogen peroxide is electrically charged, which is not the usual experience of chemists.

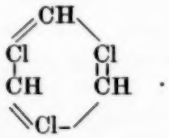
The main thesis Friend develops in connexion with complex ammines and allied compounds. In his most recent publication (this vol., p. 715) he lays particular stress on the supposed vagueness of some of Werner's assumptions. In the case of hexammine cobaltic chloride, $[Co(NH_3)_6]Cl_3$, for example, Friend refers to the fact that "the dissociable chlorine atoms hover in an indefinite manner round the nucleus as a whole, and are not attached to any particular point on or within it." He considers, however, that a cobalt atom can be "surrounded" by a "shell" of groups or atoms in such a way that it cannot escape. How it is held, unless the shell "exerts merely a general attractive force akin to that of gravity" one is left to imagine. As he does not give one any idea as to the dimensions of cobalt atom and shell, the statement that the cobalt atom in the shell "cannot easily escape for purely physical reasons" is not convincing.

In short, Friend substitutes for a loosely defined ionisable region an equally ill-defined, non-ionisable region.

His comparison of an ammine shell with a Kohlrausch "watery atmosphere" is instructive, although in the case, say, of potassium

chloride, where we probably have such an "atmosphere," it is the ion that collects water molecules after it has been produced by the process of dissolution, and the electrical charge seems the cause of such an attraction of solvent molecules.

In his last communication (p. 716), Friend refers to tervalent chlorine as the usual form in which combined chlorine is to be found. Yet in another sentence he advocates an adherence to "definite valency values," and he obviously alludes to those of the organic chemist. Until we are able to isolate a compound of such a type as:

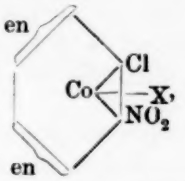


it seems rather premature to consider chlorine a tervalent element, at least in a ring-forming capacity. It is not because of strain in such a ring as that just depicted that Friend could suggest its impossibility, for in none of his publications does he take into account the well-known facts in connexion with Baeyer's strain theory or its modifications.

The strong point of Werner's theory is the definite proof that the six co-ordinated atoms or groups have a more or less well-defined, octahedral orientation. Unless Friend's "shell" is identical with Werner's octahedral structure, there is no explanation on the cyclic theory of the existence of optical activity among certain types of compounds. Werner's theory, on the other hand, admits the present lack of knowledge in connexion with valency by assuming the cobalt atom to be situated within its octahedral environment much as a carbon atom is situated in its tetrahedral environment. Werner does not imagine a "valence" extending from the cobalt atom to each of the corners of the octahedron, and so escapes the criticism of the strain theorists. Friend apparently ignores the effect of bridged linking in a six-membered ring. In one case (hexammine cobaltic chloride) he abandons the definiteness which characterises his use of lines for valencies, and pictures the cobalt atom as being simply "retained" by a shell of loosely-bound ammino-groups. Some sort of indication as to the position in space occupied by the groups or atoms constituting the shell is obviously necessary.

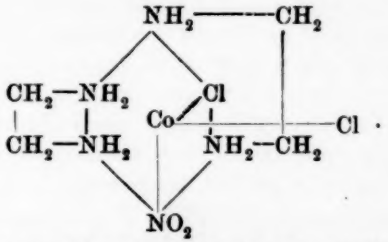
When one considers the type $\left[\begin{matrix}Cl\\O_2N\end{matrix}\ Co\,en_2\right]X$—chloronitrodiethylenediammine cobaltic salts—one again fails to see the applicability of the "cyclic" theory. It cannot actually be disputed that the groups situated on Werner's octahedron are the groups con-

stituting Friend's shell. The above type must therefore be written on the cyclic theory:



(to take the "ortho"-compound). Here it seems very difficult to see how to dispose of the valencies of the nitrogen atom in the nitro-group. From the present author's attempts to arrange the various available kinds of valency, the conclusion arrived at is that the nitrogen atom retains a free negative valency, which seems unsatisfactory.

It must be pointed out that to conceive of Friend's "meta"-type in this particular instance is almost impossible; it would have to be written:



We have also to consider the arrangement of the valencies in a ring composed of NH_3 groups. Ordinary theories of the quinquevalent nitrogen atom fail to indicate a possibility of arranging NH_3 groups in stable rings, although attempts have been made (see Stewart, "Recent Advances in Physical and Inorganic Chemistry," 1909, p. 102) to justify the Jörgensen ammine formulæ by discussing possible constitutions of di- and tri-hydroxylamine salts; in the latter cases the α-nitrogen atom is combined with a positive atom (hydrogen) and the ω-nitrogen with a negative atom or group, for example, chlorine. Each intermediate NH_3 group simply has to exert a pair of positive and negative valencies. Here we have a definite expectation of stability, since hydrogen and chlorine are so different in nature. In an ammine ring of the type suggested by Friend, however, one cannot expect stability, since the individual component groups are so similar one to another. Friend refers to the analogy between metalammines and ring compounds of carbon, but he seems to overlook the fact that unless some strong salt-forming influence is at work, nitrogen atoms do not combine together in the way that is so characteristic of carbon.

In the case of the nitroprussides, Friend suggests a double formula. A molecular-weight determination or, better, a determination of the number of ions by the conductivity method, is necessary before such a formula can be accepted. The author hopes to examine these points when time is available for experimental work.

With the complex cyanogen compounds, Friend assumes the possibility of quinquevalent nitrogen at once, (*a*) being united by a treble bond to carbon, (*b*) being part of a ring, and (*c*) having still acidic properties and combining with potassium. One cannot exclude such a system as this because of its uniqueness merely, but Friend's theory suggests the possibility of replacing one of the hydrogen atoms in, say, ammonium chloride by potassium, NH_4Cl giving NH_3KCl, which is not the case.

Secondly, there seems to be no need for a theory accounting for the existence of isomeric ferrocyanides, since sodium α- and β-ferrocyanides are identical, not isomeric.*

Finally, it is almost impossible to conceive in space of the arrangement suggested by Friend for Prussian-blue. It is the use of definite valency bonds that seems to be the chief disadvantage of Friend's theory; for one cannot but conclude that such ring-compounds can be classified among heterocyclic compounds, and it has frequently been shown that these obey strain-laws similar to those established for carbon compounds.

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[*Received, August 1st*, 1916.]

LXXXIII.—*Molecular Weight Determinations in Bromine by the Air-current Method.*

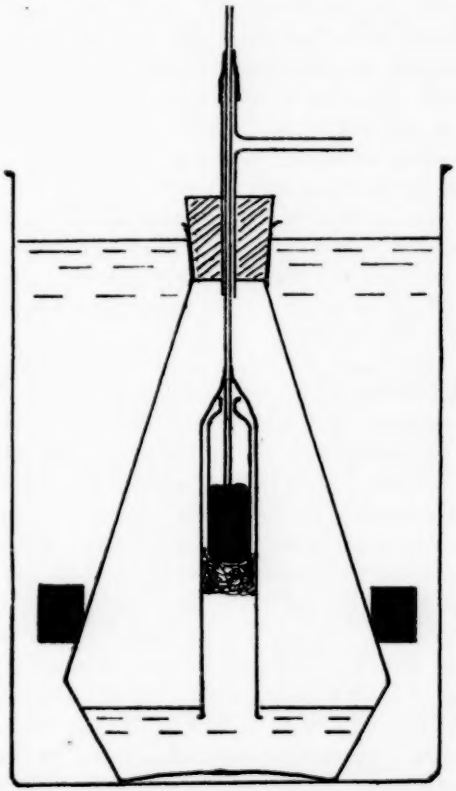
By ROBERT WRIGHT.

BECKMANN (*Zeitsch. anorg. Chem.*, 1906, **51**, 96) has made use of bromine in both the cryoscopic and ebullioscopic methods of molecular-weight determination, and has shown it to be a valuable solvent in the case of many inorganic substances. It is not, however, an altogether suitable medium, as the great chemical activity of the liquid and its vapour prohibits the use of any cork or rubber connexion in the construction of the apparatus in which it is contained, whilst the irritating nature of the fumes constitutes a further bar to its employment.

* Private communication from Mr. G. M. Bennett.

In the apparatus here described for the measurement of vapour pressure by the air-current method, the bromine vapours can only come in contact with glass or with the absorbing solution, so that no contamination can take place and, since there are no connexions of any kind, escape of the fumes is impossible.

A half-litre conical flask containing about a gram of potassium iodide dissolved in 30 c.c. of water, is immersed by means of a



heavy lead ring in a large beaker filled with water at the temperature of the room. As a determination is easily completed in half an hour, the beaker and its contents form a quite efficient thermostat. The flask is closed with a rubber stopper, through which passes a glass tube fitted with a side-piece, as shown. A fairly wide tube of about 20 mm. diameter and 12 cm. long is closed at one end, through which is sealed a tube of 3 or 4 mm. external diameter. This inner tube is about 25 cm. long, and projects axially

into the wider tube for a length of 6 cm. The wide tube must be capable of introduction into the flask, whilst the upper end of the inner tube must be able to pass through the vertical limb of the T-piece with which the stopper is fitted. The inner tube and T-piece are joined together by a short length of rubber tubing.

The solute and bromine are contained in a small stoppered bottle of about 10 c.c. capacity and of a diameter slightly less than that of the wide tube. After weighing, the stopper is removed and the bottle inserted in the wide tube, so that the inner tube extends almost to the bottom of the bottle, which is then secured in position by means of a plug of glass-wool. There should be a distance of 3—4 cm. between the plug of wool and the open end of the tube, for the latter is kept below the surface of the potassium iodide solution during an estimation, and it is highly important that the glass-wool should not become wetted.

In carrying out a determination, the solute and bromine are weighed out in the bottle, which is then fixed in position. The apparatus, apart from the flask, is next placed in a retort clamp and left for half an hour, the flask being meanwhile immersed in the thermostat. This waiting is essential in order to allow the bromine, which has been slightly warmed by handling, to cool to the temperature of the room. The apparatus is now inserted in the flask, and the level adjusted so that the open end of the wide tube dips just below the surface of the potassium iodide solution. The side-tube of the T-piece which passes through the rubber stopper is then connected with an aspirator which is fitted with a manometer. Neither aspirator nor manometer is shown in the figure. The aspirator tap is next carefully opened, and the pressure inside the apparatus reduced until the first bubble of air passes through the bromine. The tap is then closed, and a 200 c.c. graduated flask placed under it, when it is again opened and the water allowed to drip out at a rate which will fill the flask in about twenty-five minutes. As the inside of the measuring flask is usually wet at the beginning of an estimation, it should be calibrated in that state by running into it 200 c.c. of water from a pipette or burette. When the level of the water in the flask has reached the graduation mark, the tap of the aspirator is closed and the pressure as shown by the manometer and the temperature of the thermostat noted. The apparatus is now disconnected, care being taken that the solution adhering to the end of the wide tube is washed down into the flask, and the liberated iodine titrated by means of $N/10$-sodium thiosulphate. From this result the weight of bromine carried over by the air-current can be directly calcu-

lated, and the vapour pressure determined by means of the expression:

$$P = \frac{wv(273+t)B\,760}{273pV+wv(273+t)760},$$

where P = vapour pressure required.
B = barometric height in mm.
p = pressure of air in aspirator, $= B -$ (manometer reading + vapour pressure of water at t^c).
t = temperature of air in the apparatus.
V = volume of air aspirated in litres, $= 0{\cdot}2000$.
v = specific volume of bromine vapour in litres $= 22{\cdot}4/$mol. wt. $= 0{\cdot}1400$.
w = weight of bromine obtained.

The results obtained for pure bromine are shown in comparison with those calculated by interpolation from figures by Ramsay and Young in the table on p. 1138.

Temperature.	V.P.	R. and Y.
16·3°	144·3 mm.	144·5 mm.
16·7	147·2	148·6
19·2	164·3	166·0
20·4	173·4	175·0

Although a high degree of accuracy cannot be claimed for the air-current method, still it was thought advisable to base all calculations on the measurements so obtained, as errors involved in the process are to a certain extent eliminated in comparative measurements. Therefore, in the following molecular-weight determinations the vapour pressure of pure bromine is taken from the straight-line curve obtained by plotting the logarithms of the above vapour pressures against their corresponding temperatures. The data and the calculated results are given in the table; the molecular weights being derived from the usual formula for the lowering of the vapour pressure:

$$M = \frac{P'Sm}{(P-P')s},$$

where M and m are the molecular weights of solute and solvent, S and s their weights in grams, P the vapour pressure of the pure solvent, and P' that of the solution.

The preparation of the substances calls for no special mention. The bromine was purified by redistillation; the tin and antimony bromides were prepared by dropping bromine on samples of the pure metals weighed out in the small bottle used in the determinations, the bottle being carefully cooled after the addition of each drop of bromine; the solutions of iodine bromide and sulphur were obtained by simply dissolving iodine and sulphur in bromine.

Table of Molecular Weights of Substances Dissolved in Bromine.

Substance.	*S.*	*s.*	*B.*	*p.*	*m.*	*t*°.	*w.*	*P.*	*P′.*	(Found.) *M.*	(True.) *M.*
Bromoform	3·5895	11·767	762	739	92	18·7	0·2784	160·7	134·5	252	253
,,	3·5895	11·489	762	739	92	18·7	0·2768	160·7	134·5	252	—
,,	2·5330	14·476	755	733	102	18·1	0·2976	156·5	141·5	264	—
,,	2·5530	14·166	755	732	93	18·1	0·2936	156·5	140·0	243	—
Antimony tribromide	2·9079	13·589	770	747	95	17·9	0·3040	155·0	145·0	394	360
,,	2·9079	13·205	770	747	93	18·1	0·3040	156·5	145·0	350	—
Stannic bromide	3·485	14·05	764	743	80	18·9	0·3176	162·2	149·5	467	439
,,	3·485	13·50	764	743	78	18·9	0·3200	162·2	150·0	486	—
Sulphur	0·2385	14·690	770	749	87	16·8	0·2944	148·0	139·7	61	64
,,	0·3285	14·390	770	749	87	16·8	0·2944	148·0	139·7	61·5	—
,,	0·3920	12·660	770	749	78	17·7	0·3080	153·8	142·4	62	—
,,	0·3920	12·360	770	749	78	17·7	0·2984	153·8	141·8	60	—
Iodine monobromide	0·4648	14·056	765	743	78	18·4	0·3320	158·5	154·8	221	207
,,	0·4648	13·724	765	743	81	18·4	0·3312	158·5	154·5	209	—
,,	0·4292	14·280	765	743	80	18·3	0·3232	157·0	151·5	215	—
,,	0·3225	14·232	765	741	80	20·1	0·3416	170·2	159·6	227	—

Volume of air aspirated = 200 c.c. in each determination.

S = weight of solute. s = weight of solvent. B = barometric height. P = pressure of air in aspirator. m = manometer reading in mm. of water. w = weight of bromine obtained. P = vapour pressure of solvent. P' = vapour pressure of solution. t = temperature.

From the results obtained it will be seen that only one atom of antimony, tin, or iodine is contained in the molecule of the bromide, and although a molecular-weight determination does not give very definite information as to the amount of solvent combined with the solute, still, it is probable that the usually accepted formulæ are correct. The case of sulphur is of interest in that the solute seems to exist as simple diatomic sulphur molecules uncombined with the solvent, or, if combined, it must exist as a compound of the nature S_2Br_2, the molecule of which contains two atoms of sulphur. The production of a compound by the simple solution of sulphur in bromine is, however, very improbable, as the preparation of sulphur bromide requires the digestion together of the two elements for some time at a temperature of 100° (Ruff and Winterfeld, *Ber.*, 1903, **36**, 2437). Moreover, the compound so obtained is very unstable, and is readily decomposed by the moisture of the atmosphere with the evolution of hydrogen bromide. An attempt was made to prepare and determine the molecular weight of sulphur bromide, but the result was unsatisfactory, as the compound decomposed rapidly as soon as the tube in which it was prepared was opened to the atmosphere.

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[*Received, September 12th*, 1916.]

LXXXIV.—*The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. Part XXI. The Relationship of the Rotatory Powers of Ethyl Tartrate,* iso*Butyl Tartrate and* iso*Butyl Diacetyltartrate.*

By THOMAS STEWART PATTERSON.

IN a paper published some years ago (T., 1913, **103**, 145) an attempt was made to develop a suggestion regarding the temperature–rotation curves of active substances, whereby the data for different compounds, derivatives of each other, or of one or more related active substances, under different conditions—in solution, for instance—could be brought into harmony. The argument was, briefly, as follows:

In the first place it was to be expected that the rotation data for two related active substances must be connected in some way,

however obscure, but, before any connexion can be recognised, conditions must be discovered under which the rotations of the compounds are comparable. It was suggested that the maximum which often occurs in temperature–rotation curves, a singular point which can be recognised, might form a basis from which the problem could be attacked. It was shown that in a series of closely related compounds, such as the esters of tartaric acid, the maximum rotation occurs at different temperatures and at different rotation values, the comparatively slight change of composition which occurs, for instance, when an ethyl group is displaced by an *n*-propyl group, causing a slight displacement of the maximum rotation. Again, the effect of solution in the case of ethyl tartrate is to displace this maximum towards a lower temperature and a higher value in certain solvents, and towards a higher temperature and a lower value in others. It was then noticed, this being indeed the observation which led to the generalisation, that the temperature–rotation curves for the ethyl and *iso*butyl esters of di-trichloroacetyltartaric acid had minimum values at definite temperatures, and that these minima moved, on solution in certain solvents, in the same direction as does the maximum in ethyl tartrate. The last observation suggested the idea that just as the slight change in constitution involved in the displacement of an ethyl group by an *n*-propyl group brings about a slight shift of the maximum rotation, so the substitution of one of the hydroxylic hydrogens of the ester by the trichloroacetyl radicle—presumably a much greater change of constitution—has produced a very much greater displacement of the temperature–rotation curves, the maximum being removed from the region of ordinary temperatures altogether and a minimum value brought into view, that is to say, a part of the curve which, in homogeneous ethyl tartrate, the parent substance, is probably to be found only at a high temperature.

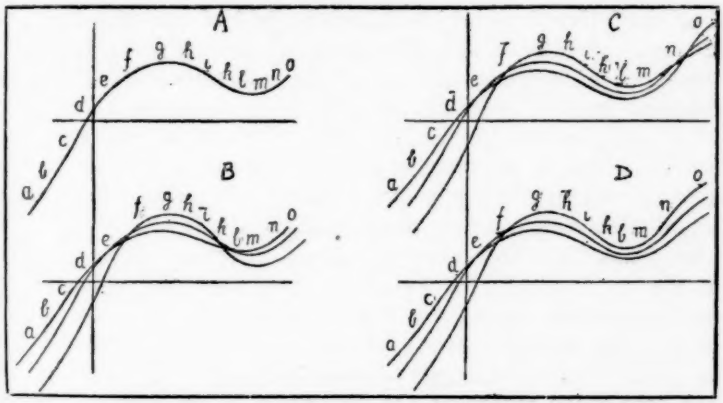
This was further corroborated in a striking manner by the temperature–rotation curves for ethyl tartrate in quinoline. In this solvent a minimum rotation had been observed for a dilute solution, $p=10$, and it appeared possible that the influence of quinoline on the simple ester was so great as to shift the maximum rotation out of the region of ordinary temperatures altogether, and thus to bring into view the minimum which, in the homogeneous ester, would be found at the high temperature. A powerful solvent like quinoline would thus have an effect somewhat similar to that produced by a considerable change of constitution (see Fig. 2).

The idea thus developed was, that for some fundamental substance such as tartaric acid, the temperature–rotation curve, if it could be determined over a wide enough range of temperature,

would probably show several maximum and minimum values, and that the temperature–rotation curve for the acid in some solvent, determined in a similar manner, would also show a number of maxima and minima corresponding with, but occurring at different temperatures and having, presumably, different values from, those for the homogeneous substance. Similarly, the temperature–rotation curves for a derivative of tartaric acid would resemble that for the parent substance in showing maxima and minima, which, again, would occur at different temperatures and have different values, preserving, however, as before a general resemblance.

The curve *A* in Fig. 1 represents this idea in the case of ethyl tartrate for, say, sodium light, if the rotation of the ester could be examined over a range of temperature between perhaps −100° and

FIG. 1.



+400°. The known behaviour of the ester is represented by the part of the curve marked *cdefgh*, and the suggestion is that on further heating a minimum would be found, as in the part of the curve marked *klmn*, whilst on cooling to a low temperature another minimum would be found to the left of *a*. In the meantime the further course of the curve need not be discussed.

When the ester is dissolved in a liquid which does not much alter its rotation, the form of the graph within the range of ordinary temperatures is known to be closely similar to *cdefgh*; if the solvent has a powerful elevating influence, like nitrobenzene, for example, the shape of the curve gradually alters as the concentration of the active substance diminishes, starting, of course, from that for the homogeneous compound, and changing from solution to solution from the form *cdefgh* to *efghi* to *ghik* in the most dilute

solution. This gradual development of shape must be carefully noticed; the curve for any particular solution is not to be regarded as something suddenly arrived at, but rather as the result of a process of evolution from an original form. If the influence of the solvent is yet more powerful, as in quinoline, the change in shape of the graph proceeds still further until the part *iklm* is brought into view. On the other hand, if a solvent with a powerful depressing influence be used, for example, *s*-tetrabromoethane, the graph alters in the opposite direction, and even at fairly high temperatures only the part *cdef* has been observed.*

The ideas just described were entirely the result of investigations in which sodium light had been used, but it was shown that when they are applied to the rather small amount of really comprehensive work which had been done with light of other colours, they immediately introduced a very satisfactory harmony and afforded a point of view from which the whole field of optical activity—the influence of constitution, the effect of temperature change, the behaviour of solvents, the variations introduced by the use of different colours of light—can readily be grasped. Thus it was pointed out that what is generally called anomalous rotation-dispersion is due to the fact that the temperature–rotation curves for different colours of light for a given substance are somewhat retarded on each other or occur in slightly different phases, in such a way that they intersect over a range of temperature, as is shown in Fig. 1, *B*, at *ef*. It was also shown that the region of intersection of these curves was displaced as the result of solution, in very much the same way as is the maximum rotation itself, this being. of course, a very strong confirmation of the induction which had been made regarding the behaviour of the point of maximum rotation.

It is one of the most valuable qualities of these suggestions that they give a very clear indication of the direction in which further investigation is desirable, and it is obvious that they might be further tested and verified by an examination with light of various different refrangibilities, of some of the most interesting cases previously considered, especially of those which had proved most perplexing. With this end in view, therefore, three active compounds, closely related to one another, have been examined for six or more colours of light over a wide range of temperature in the homogeneous state and in solution in several solvents.

A few experimental details may first be mentioned, especially in

* It is best to suppose the axes fixed and then to imagine the whole curve moved past these to the right or left and upwards or downwards, as the case may be.

regard to the method of obtaining the various colours of light used. A large Schmidt and Haensch polarimeter is fitted with a direct-vision spectroscope by the same makers, having adjustable slits at each end, the end nearer the source of light being controlled by a graduated screw, in such a way that light of any particular wave-length, selected from the enclosed mercury arc or other source, can be passed into the polarimeter. It is possible with this arrangement in ordinary cases to read the mercury line, usually called violet, 4358·3, using a half-shadow angle of only one degree,* whilst, of course, the green, 5460·7, could be read with still greater accuracy. Further, the two mercury yellows can easily be read separately, with a half-shadow angle of one degree. The instrument was so arranged that the half-shadow angle could be adjusted to one degree or four degrees as might be required. The lines taken from the mercury arc were usually the violet, the green, and the yellow, 5790·5.

Light of other colours was obtained from a Nernst lamp. In some of the earlier experiments the wave-length of the light passing through the instrument was regulated simply by the graduated screw, which had been calibrated by the makers. It was feared, however, that this was not sufficiently accurate, and the following arrangement was finally adopted. The light from the Nernst lamp, after passing through the direct-vision spectroscope on its way to the polarimeter, was deflected by means of a small, movable, comparison prism to a Hilger spectrometer. At the same time, light direct from the mercury arc was passed, by means of mirrors, also into the Hilger spectrometer, in such a way that a little parallelopiped of approximately monochromatic light from the direct-vision spectroscope was seen superposed on the mercury arc spectrum. By adjusting the screw of the direct-vision spectroscope, the light passing through the latter may be made to correspond exactly with any of the lines of the mercury spectrum, and, of course, could easily be adjusted, if desired, to correspond with any other line, such as lithium red. By this method a high degree of accuracy in the adjustment of the apparatus for light of any particular wave-length may be secured, and the apparatus is under constant control. It is true that such light is not absolutely homogeneous, but since its optical centre can be made to correspond exactly with that of the monochromatic light desired, and the brightness is much greater than can be obtained from most homogeneous sources, such as lithium or thallium flames, it is probable that the accuracy of the method is greater than could be attained to by the use of these direct sources.

* Compare Lowry, T., 1913, **103**, 1064.

In this way three other colours of light were obtained. One corresponded with the light blue of the mercury spectrum, 4959·7 *; the second corresponded with the red line of the mercury arc, 6234·3; and the third with a faint red line in the mercury arc, 6716·3. This last line may be regarded, for all practical purposes of comparison, as identical with lithium, 6708. In some cases readings were taken with light corresponding with the mercury line, 6907·5, but as this could be read only with some considerable difficulty, it was abandoned in favour of light of wave-length 6716·3. In the sequel and on the diagrams the six lines first mentioned will be denoted as follows:

Mercury Lines.

r_1, 6716·3	g, 5460·7
r_2, 6234·3	b, 4959·7
y, 5790·5	v, 4358·3

In cases where other colours were used the wave-length will be quoted.

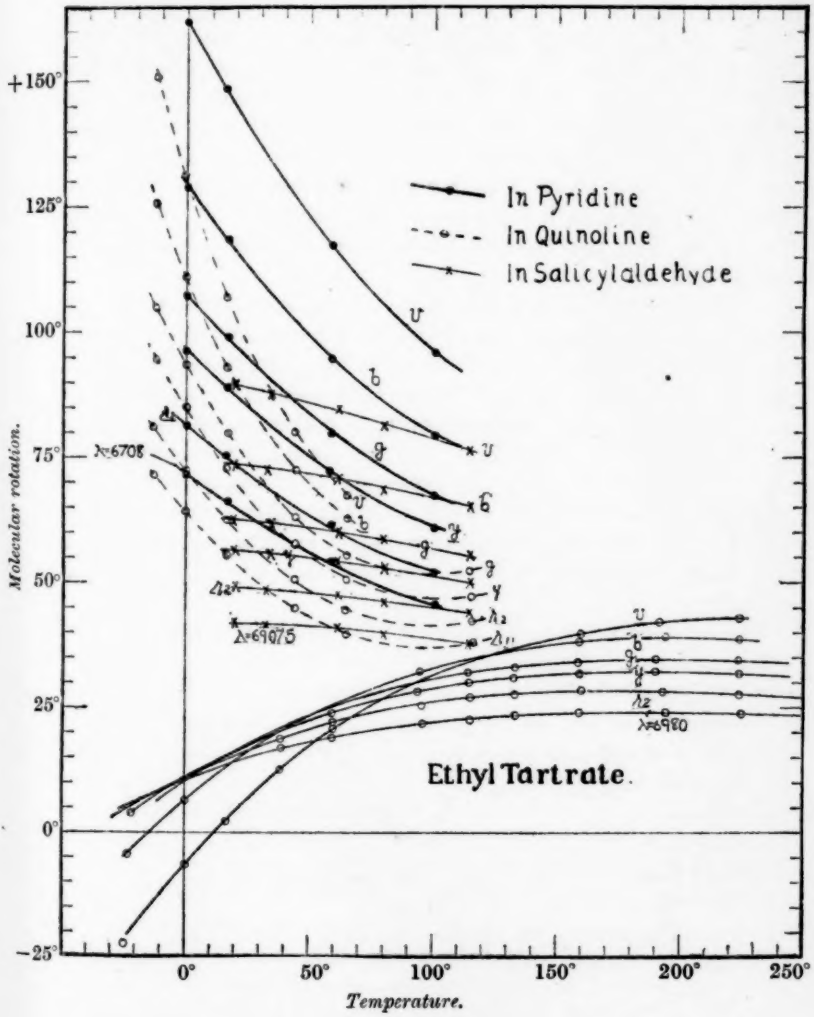
In an attempt further to develop the ideas outlined above, the matter which first claims attention is the investigation, with the assistance of rotation-dispersion, of the ethyl tartrate temperature–rotation curves as far as possible beyond the maximum value either directly or indirectly, in order to obtain any possible information bearing on the existence of the high-temperature minimum, and to ascertain the nature of this minimum. By the nature of the minimum is meant the sequence, in that neighbourhood, of the rotation values for the different colours of light. Generally speaking, the data hitherto obtained suggest that at a maximum the absolute value of the rotation is greatest for violet and least for red, whereas at a minimum the opposite is the case, the absolute value for the rotation being least for violet and greatest for red. If this were the case in the present instance, it would follow of necessity that in order to arrive at this condition of affairs the different curves should intersect each other between the maximum and the minimum values, and this would probably give rise to a second region of visibly anomalous rotation-dispersion. Since the curves do, in fact, cut each other before the maximum is reached, that is, at fairly low temperatures, there is nothing inherently improbable in their cutting again beyond the maximum. Fig. 1, *B*, therefore represents, in a qualitative fashion, what might perhaps be regarded as, a priori, the most likely behaviour.

In order to examine this point as far as possible by direct means,

* This line can be read directly from the mercury arc, although it is rather faint to be of much use.

the rotation of ethyl tartrate was determined for eight different colours of light, up to temperatures of about 230°. The data are given at the end of the paper, and those for molecular rotation

FIG. 2.



are plotted in Fig. 2,* in regard to which in the meantime, however, little need be said. It will be noticed that the curves intersect in the manner which is now familiar, that they reach maxima

* To avoid confusion only six of the eight curves are shown.

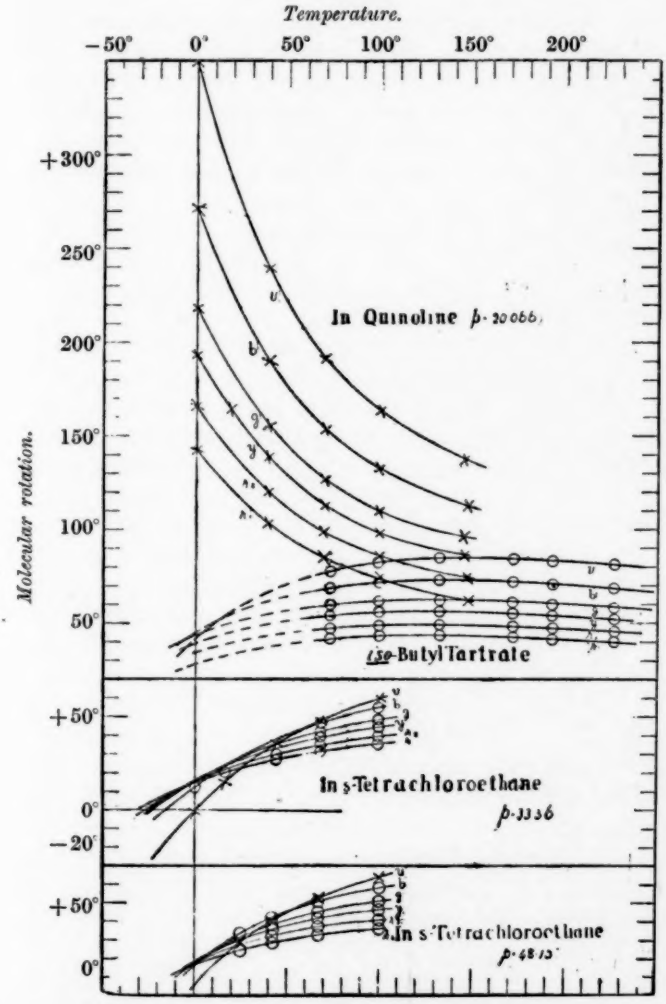
at different temperatures for the various colours—the maximum for violet, however, not yet being reached—and then fall again. It was not, however, found possible to examine ethyl tartrate with success above 230° or thereby, and there is certainly little hope, meanwhile, of continuing the investigation in such a way as directly to decide the point at issue. Already at 227° the liquid began to boil out of the tube, and on long heating at this high temperature it darkens in colour. It will be noticed, however, even from these curves, short as they unfortunately are, that there is apparently not much tendency for them to run together again. Whereas on the left of the maximum the curves actually intersect, to the right of the maximum they show no apparent signs of doing so. They look rather as if they might run parallel. For the moment that is all that can be said about them in this connexion; they will be referred to again later on.

Direct observation thus failing, it is necessary to resort to indirect methods. It was shown in a former paper that the temperature of maximum rotation in the case of *iso*butyl tartrate is lower than that for ethyl tartrate, and therefore it seemed probable that the *iso*butyl tartrate temperature–rotation curves could be examined further beyond the maximum than was possible for ethyl tartrate, especially, of course, since the boiling point of the former is higher. Then since the behaviour of the different esters of tartaric acid is similar, any characteristics which the curve for *iso*butyl tartrate may show might reasonably be expected to apply to ethyl tartrate as well.

The rotation of *iso*butyl tartrate was therefore examined for six different colours of light, and the results as regards molecular rotation are shown in Fig. 3. The maximum rotation is apparent in all these curves, and, as in the case of ethyl tartrate, we find both that the maximum moves to a higher temperature in passing from red to violet and that, whilst at low temperatures the curves clearly tend to cut one another, at high temperatures it seems most probable that they would run more or less parallel. It is, at least, apparent from the direction of the curves that they could scarcely be expected to intersect at any temperature at which, at present, observations could be made. It may be inferred, therefore, although, of course, only tentatively, from the behaviour of both these esters, that the temperature–rotation curves are somewhat different at low and at high temperatures. At the former there is intersection, but at the latter there is no definite evidence of this being the case, but rather an indication that they may run parallel. So much can be arrived at from observations on the homogeneous esters.

It is therefore necessary again to resort to indirect evidence, namely, that supplied by the use of different solvents, and the bearing of such evidence will be clearest by considering the data for the rotation of *iso*butyl tartrate at temperatures below about

FIG. 3.



60°, first in the homogeneous condition and then in solution in *s*-tetrachloroethane. The temperature–rotation curves for homogeneous ethyl tartrate intersect at moderate temperatures over a fairly wide range, Fig. 2, and therefore it may be assumed without

hesitation that the corresponding curves for *iso*butyl tartrate would intersect in a similar manner, but at temperatures at which, on account of the ready solidification of the ester, direct determination is not possible, and it will be apparent from the trend of the curves that the intersection of, say, the violet and the blue would occur at a temperature in the neighbourhood of 15°. It has also been remarked that in a solvent with a sufficient depressing * influence, the maximum rotation is moved towards a higher temperature but towards a lower rotation value, and that, further, the intersection of any two given curves is moved, on solution, in a similar manner. Therefore, if *iso*butyl tartrate be dissolved in a solvent of depressing influence we might expect to find that, in the solution, the intersection of any two given curves and, of course, the whole region of visibly anomalous rotation-dispersion as well, would occur at higher and higher temperatures the greater the influence of the solvent, and, for any such solvent, at a higher temperature the less the concentration.

Now *s*-tetrachloroethane is, with regard to ethyl tartrate, a solvent of this character, and is thus likely to have the same effect on *iso*butyl tartrate. A solution of *iso*butyl tartrate in this liquid ($p=48{\cdot}15$) was therefore made up and examined over a range of temperature. The result is shown in Fig. 3 (lowest diagram). It will be noticed at once that at any given temperature, say, 100°, the rotation values for all the different colours of light are less than the corresponding values in the homogeneous ester—which shows the depressing character of the solvent—and also that intersection takes place at a decidedly higher temperature than would be expected for the pure ester. Thus the curves for violet and blue intersect at 55°, those for violet and green at about 35°, and so on. The region of visibly anomalous rotation-dispersion appears, therefore, at somewhat higher temperatures. In the more dilute solution ($p=33{\cdot}362$) this is carried a little further. As shown in the table below, the intersection for blue and violet takes place at a

iso*Butyl Tartrate in* s-*Tetrachloroethane.*

Violet intersects.	$p = 48{\cdot}15$		$p = 33{\cdot}362$	
	[M]	*t*.	[M]	*t*.
b	46·7°	55°	44·5°	61·0°
g	35·5	35	35·5*	45·0
y	31·0	28	31·5	38·7
r_2	25·6	20	26·7	32·0
r_1	21·0	13	22·1	25·5

* In homogeneous ethyl tartrate violet cuts blue at +29·4° and 91°.

* One, that is to say, which lowers the rotation at the ordinary temperature.

temperature of 61°, that for violet and green at a temperature of 45°, both therefore higher than in the more concentrated solution. The region of visibly anomalous rotation-dispersion is thus passing towards the right of the diagram, and it could easily be made to pass further to the right by the use of still more dilute solutions. It is evident, therefore, that by this method we can bring into view a part of the whole temperature–rotation diagram which is otherwise not accessible, and the fact that these curves actually intersect, thus exhibiting an easily recognisable singularity, in addition to the fact that homogeneous ethyl and methyl tartrates show the same peculiarity, renders the induction which must be made all the more indisputable and definite. It is of quite particular interest to notice that the rotation values at the intersections for these two solutions are almost identical for the same pair of colours in all five cases. This is an important point which will receive consideration further on (p. 1157).

It is thus clear that a perfectly definite rotation point may be moved about as regards temperature by the use of different solvents, and, remembering this fact, we may now proceed to examine, in a similar way, the other, and for the moment more interesting, end of the diagrams for ethyl and *iso*butyl tartrates. In the case of the former ester it has been found repeatedly that certain solvents tend to move the maximum rotation to a lower temperature and a higher value. Thus, for example, the maximum rotation, $[M]_D = 30{\cdot}9°$, which occurs in the homogeneous ester at a temperature of approximately 175°, is found in a $p = 20$ per cent. nitrobenzene solution at a temperature of about 30°, and having $[M]_D = 54°$ (T., 1908, **93**, 1844). The maximum rotation has thus been moved through about 145° of temperature and raised in value by some 23°.

Taking this fact along with what has just been said as to the temperatures at which the intersection of any two curves takes place in different solutions, it seems very reasonable to conclude that an examination of the temperature–rotation curves for different colours of light for ethyl tartrate in solvents of this type at temperatures comparatively easily attainable, reveals the behaviour of the homogeneous ester at much higher temperatures. An examination has therefore been made of ethyl tartrate in a few solvents of this character, and, naturally, those were chosen which had already been found to exhibit the most marked effect.

One of these very powerful solvents is benzaldehyde, but since it has been shown in this series of researches that ortho-disubstitution often increases greatly the influence of a solvent on rotation (T., 1912, **101**, 244), it was thought that perhaps salicylaldehyde

would have an even stronger effect than benzaldehyde. A $p=20{\cdot}214$ solution of ethyl tartrate was therefore made up, and its rotation examined for six different colours of light at temperatures between 20° and 114°. It was found at once that the solvent effect had not been increased to the extent anticipated, but as representing an intermediate stage the curves obtained, which are shown in Fig. 2, may be described.

This solvent has an elevating effect approximately the same as that of water, and, on heating, the rotation diminishes, as, of course, would be expected. It is quite clear, taking these curves in conjunction with others which have been examined in the course of this investigation, that salicylaldehyde is able to shift the temperature–rotation curves for ethyl tartrate so far to the left that the region *ghi* of the curves in Fig. 1, *B*, *C*, or *D*, comes into view. The sequence of the colours is the same as it is in the neighbourhood of the maximum in homogeneous ethyl tartrate and, from their general appearance, these curves are practically a continuation of those of ethyl tartrate beyond the maximum, the only difference being that they are rather more spread out; and it may be insisted on again, as a most important point, that these curves do not assume the form shown suddenly, but as a process of evolution, starting from the shape of the curves for the homogeneous active substance and changing quite gradually as the concentration varies, until the forms shown in the diagram are reached.

A solution of ethyl tartrate in benzaldehyde, $p=10{\cdot}365$, was then examined. In order to avoid overcrowding, the curves obtained are not shown on the diagram, but they are very similar indeed to those shown for pyridine, which may be taken to represent them. The forms of the curves are different from those of salicylaldehyde. Whereas the latter are concave to the point of origin of the diagram, the former are convex; but the sequence of the rotations for the different colours of light is the same, and it seems impossible to doubt that benzaldehyde has displaced the fundamental temperature–rotation curve in such a way as to bring into view the region *kl* of Fig. 1, a part of the graph where the change of curvature actually observed would be expected. The benzaldehyde curves are thus a continuation of the salicylaldehyde curves; they enable us to explore a further region of the curve of the homogeneous ester and, corresponding with the fact that the solvent is more powerful, the curves are still further spread out and the rotations are greater. The slope downwards is much more rapid, the point of inflexion is already passed at this particular concentration, and the curvature is such as now obviously to suggest a minimum rotation at some fairly high temperature, a temperature, however,

beyond that which it would be possible to reach with a solvent of the boiling point of benzaldehyde.

Pyridine, in which a solution of ethyl tartrate of $p=19{\cdot}263$ was prepared, carries solvent influence rather further than does benzaldehyde. The behaviour is practically that which has just been described for the latter; the curves, as will be seen from the diagram, are clearly tending towards a minimum value, but the sequence of the values for the different colours of light is still the same as it is at the maximum in homogeneous ethyl tartrate. There is no sign of intersection of the curves in the manner shown at k in Fig. 1, B; there is no indication of visibly anomalous rotation-dispersion in the part of the diagram where it might have been expected, namely, in the neighbourhood of the point of inflexion; the dispersion is positive for the whole range of temperature over which the curves were examined, and the temperature-rotation curves appear to tend to run parallel at higher temperatures; they look, in fact, as if they might all reach distinct minima somewhere about the same temperature, but without any intersection. A satisfactory decision as to what happens in the neighbourhood of the minimum could only be arrived at by an examination of curves actually exhibiting the minimum, and this requires a still more powerful solvent.

Quinoline is such a solvent, and at a comparatively early stage in these researches (T., 1909, **95**, 323) the curves which were found for ethyl tartrate in quinoline showed quite clearly a minimum rotation for yellow light at temperatures just above 100°. This at the time was difficult to interpret, but later on its significance became plainer. Two solutions in quinoline were therefore examined, and on Fig. 2 the curves for that of $p=13{\cdot}601$ are shown. From these curves it is clear that the maximum value has passed far out to the left and the minimum becomes apparent. The dispersion is positive, as in the homogeneous ester at the maximum, whilst the powerful character of the solvent is shown by the great spreading of the temperature-rotation curves and also by their steepness at low temperatures. It is very disappointing, however, that here, although the minimum is actually brought into view at a temperature of only 100°, and the fairly high boiling point of quinoline would permit of the experiments being carried to a much higher temperature, these curves cannot, in fact, be further followed because the solution darkens so much just above 100° that the rotations can no longer be read.

Nevertheless, these curves for quinoline appear to prove conclusively that the temperature-rotation curves for ethyl tartrate do not intersect before the minimum is reached, and, therefore, that they

do not correspond with those shown in Fig. 1, *B*. Thus it seems clear that intersection does not necessarily take place on both sides of the maximum.

In order perhaps to get out towards a more distant portion of the curves, *iso*butyl tartrate was then examined in quinoline solution. The data are represented in Fig. 3. It will be seen that here the temperature–rotation curves are now spread out more than in the case of ethyl tartrate, and that, on the whole, the rotations are higher; much higher in the violet, the slope of the curves being very steep. Unfortunately, the minimum lies at a higher temperature than in the ethyl ester, and it was found impossible to get beyond it, since darkening occurred in this case also, although at somewhat higher temperatures than for ethyl tartrate.

From these experiments with quinoline, in which the minimum in ethyl tartrate and *iso*butyl tartrate is actually reached, it may be concluded definitely that the temperature–rotation curves for these two esters do not intersect as shown at *kl* in Fig. 1, *B*. It might, however, quite well be that intersection of the curves would occur after the minimum has been passed, in the manner shown at *n* in Fig. 1, *C*. It is particularly regrettable that the experiments in quinoline could not be carried to a sufficiently high temperature to enable a conclusion in regard to this point to be reached.

Happily, further indirect evidence is available. As has been mentioned already, ethyl and *iso*butyl di-trichloroacetyltartrates exhibit minima in their temperature–rotation curves, and it was suggested that these minima correspond with those which may be expected to exist in ethyl tartrate or *iso*butyl tartrate at a high temperature, and actually do exist in solutions of these substances in quinoline at about 100°. If this be the case, the change of constitution in passing from the simple to the acyl ester has shifted the whole temperature–rotation curve to the left, in such a way that the minimum comes into view, just as solution in quinoline shifts the curves for the simple esters to the left, making the minimum apparent.

The rotation of *iso*butyl diacetyltartrate, which is a liquid and therefore can be studied over a wide range of temperature, was then examined in order to ascertain whether its rotation can be linked up with that of *iso*butyl tartrate in the homogeneous condition or in solution. If the minimum in the undiluted acyl ester really corresponds with that for *iso*butyl tartrate in quinoline, then the sequence of the rotation values—which, as has already been remarked, is somewhat unusual, being least for red and greatest

for violet—before or at the minimum should be the same as for *iso*butyl tartrate in quinoline. Further, if the sequence be the same, thus helping to prove the identity of these minima, the subsequent course of the curves may be taken to indicate the behaviour of the simple ester at temperatures still higher than that at which its minimum occurs. There should also be no intersection of the curves before the minimum is reached.

The data for *iso*butyl diacetyltartrate are represented by the curves of Fig. 4, and it will be noticed in the first place that the requirements mentioned are realised. The sequence of the rotation values is the same as for homogeneous *iso*butyl tartrate at the maximum, or in quinoline before or at the minimum; in other words, the dispersion is positive. The curves show a distinct minimum for all the different colours of light. That for violet occurs at a temperature of about 50°, for blue about 55°, for green about 59°, for yellow and red about 73°, and for $\lambda=6742$ about 82°. The minimum rotation thus moves to a higher temperature and a lower rotation as the wave-length of the light used increases. In this respect it differs from the maximum in homogeneous *iso*butyl tartrate, which moves in the opposite way.

Again, the curves show no intersection before reaching their minima; there is in that region no occurrence of visibly anomalous rotation–dispersion, and, further, the curves do not cut one another or even tend to cut one another after the minimum value has been reached; they proceed to rise again, spreading out at the same time, presumably to reach a new maximum at some higher temperature.

Thus by piecing together the evidence obtained from the behaviour of homogeneous ethyl tartrate and *iso*butyl tartrate, the behaviour of these esters in quinoline, and the behaviour of the diacetyl derivative of *iso*butyl tartrate in the homogeneous condition, it may be concluded that if ethyl tartrate or *iso*butyl tartrate could be examined over a wide range of temperature the whole course of the curves would correspond with the behaviour shown in Fig. 1, *D*, where we have first a region of visibly anomalous dispersion, then a maximum, followed without further intersection by a minimum, whereupon the curves rise to another maximum, up to which, in the meantime, we cannot follow them.

Now just as it has been shown to be possible to develop the temperature–rotation curves for an ester like ethyl tartrate, by means of solvents, in such a way as to be able to examine their characteristics in regions which are inaccessible to direct observation, it is natural to apply this same process to *iso*butyl diacetyl-

tartrate, first in order to link up its curves with those of the homogeneous ester, and secondly to try if possible to get out to this new maximum.

If a series of solvents had exactly the same effect on *iso*butyl diacetyltartrate as on ethyl tartrate, it would naturally be expected that quinoline should shift the minimum rotation of *iso*butyl diacetyltartrate to a much lower temperature, that is, should shift the whole temperature–rotation curve to the left of the diagram, and bring into view this new maximum. Thus we might hope to get into a region beyond that which is indicated by ethyl tartrate at all, namely, towards *o* in Fig. 1.

Solvents of the opposite type, such as *s*-tetrachloroethane, might be expected to move the minimum towards high temperatures, and to bring into view the maximum which is to be expected in this ester at low temperatures, the maximum corresponding with that actually found in ethyl tartrate.

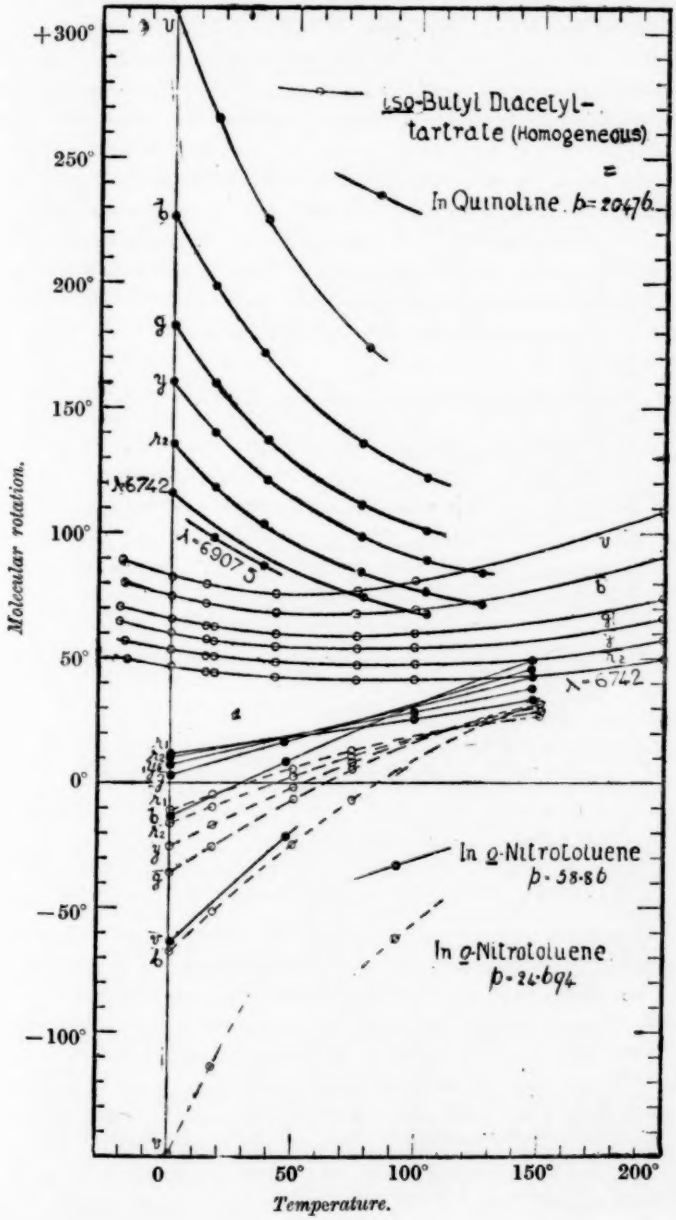
The solvent influence of quinoline on *iso*butyl diacetyltartrate was first examined. The results are shown in Fig. 4, and it is obvious at once that the solvent effect is great. At low temperatures the rotation is much raised, from about $[M]^0_g + 64°$ for the homogeneous ester, to about $[M]^0_g + 182{\cdot}7°$ ($p = 20{\cdot}476$), but in spite of this it is clear that the curves chiefly differ from those of homogeneous *iso*butyl diacetyltartrate in that they are very much spread out; they obviously tend to approach a minimum value, but this minimum value apparently lies at a temperature of about 200°, that is to say, decidedly higher than the temperature at which it occurs in the homogeneous ester. It therefore appears that the effect of quinoline on this ester is evident rather in the great separation of the rotation graphs than in a large displacement of the curves; and further, that such displacement as there is takes place in the opposite direction to that observed for ethyl tartrate and *iso*butyl tartrate, the minimum being moved towards a higher temperature and towards a higher rotation value. The sequence of the rotation values, the character, that is, of the dispersion, is the same as before.

That this is not due to the curves having been displaced very greatly to some new minimum is shown by the behaviour of a concentrated solution [$p = 74{\cdot}96$] of *iso*butyl diacetyltartrate in quinoline, the curves for which are shown in Fig. 5. Here the minimum rotation is only slightly shifted towards a higher value and a higher rotation, whilst the separation of the curves for the different colours of light clearly corresponds with the concentration of the solution.

As has already been mentioned, the influence of *s*-tetrachloro-

ethane might be expected to be exactly the opposite of that of quinoline. The data obtained for a $p = 20{\cdot}034$ solution of *iso*butyl

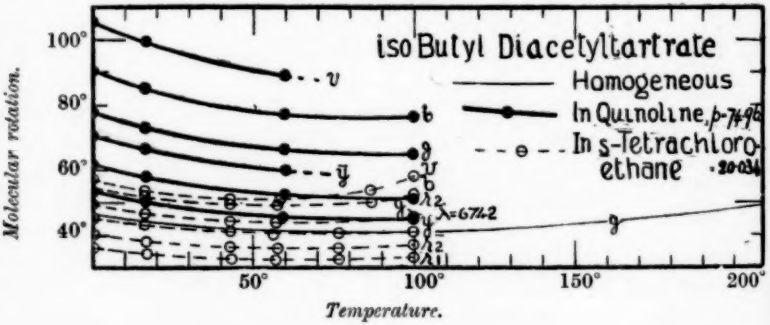
FIG. 4.



diacetyltartrate in this solvent are also shown in Fig. 5. It will be observed that the curves lie closer together than in the homogeneous ester, the opposite to what obtains in quinoline, and the minimum is shifted somewhat towards a lower temperature and a lower value. On the whole, therefore, it may be said that the temperature–rotation curves for *iso*butyl diacetyltartrate are not much shifted on solution in these two solvents, but that the solvents are acting in opposite senses, one expanding and the other contracting the curves.

Now in previous experiments (T., 1913, **103**, 152) it was found, using sodium light, that the minima in the curves for ethyl and *iso*butyl di-trichloroacetyltartrates appear to move towards a lower temperature and a lower value when these esters are dissolved in nitrobenzene, which solvent thus appears to shift these curves in the same way as it shifted that of ethyl tartrate, although with a

FIG. 5.



depression of rotation instead of an elevation. Thus, in the homogeneous condition, ethyl di-trichloroacetyltartrate shows the part *klm* of the curves in Fig. 1, *D*, whilst, on solution in nitrobenzene, the part *lmn* of the curves seems to come into view. It appeared probable, therefore, that solution of *iso*butyl diacetyltartrate in nitrobenzene would reveal the part *lmn* or *mno* of the curves, and perhaps permit of an exploration of the maximum in that neighbourhood. A solution of *iso*butyl diacetyltartrate, $p=24{\cdot}694$, was therefore made up in *o*-nitrotoluene—this solvent being chosen instead of nitrobenzene on account of its somewhat lower melting point, its behaviour otherwise being very similar to that of the latter. The results obtained are shown in Fig. 4. They are quite different from what had been expected, and they exemplify admirably the increased diagnostic value of the dispersion curves.

As was to be expected from the former experiments with the di-trichloroacetyl derivatives, the rotation is diminished by this

solvent, but in addition to this being the case it at once appears that the rotations for the different colours of light at low temperatures, instead of being in the sequence of those for the homogeneous ester or in the other solutions examined, occur exactly in the inverse order. The dispersion is negative; the rotation for violet is much less than that for red. The graphs cannot, therefore, be a continuation of the temperature–rotation curves for *iso*butyl tartrate at high temperatures, or of those of *iso*butyl diacetyltartrate on either side of the known minimum. In addition to this, however, the curvatures of these graphs—which is slight in any case—is also in the opposite sense; as the temperature rises the different curves approach one another, and, in the neighbourhood of 130°, they intersect, giving rise to visibly anomalous rotation-dispersion.

In the case of a more concentrated solution, $p=58{\cdot}86$, it will be seen that the intersection of the curves takes place in a manner similar to that observed in the dilute solution, but it is noticeable that the region of intersection, the region of visibly anomalous rotation-dispersion, is now found at a lower temperature. This, of course, indicates definitely that the whole temperature–rotation curve is not being shifted in the manner originally supposed, namely, towards the maximum at *o* in Fig. 1, *D*, but in the opposite direction, and, in addition, to a very marked extent indeed. The graphs are approaching a maximum, but it is that at *g*, Fig. 1, *D*. The curves have clearly been shifted from the region *klm* in Fig. 1, *D*, right over the maximum at *g*, so as to bring the region of visibly anomalous rotation-dispersion *ef* into view at the ordinary temperature.

This is very strongly corroborated by comparing the rotation values at which the intersections of the temperature–rotation curves for the different colours of light take place, for *iso*butyl tartrate in *s*-tetrachloroethane, on the one hand, and for *iso*butyl diacetyltartrate in *o*-nitrotoluene on the other, in the same way that the points of intersection for two different solutions of *iso*butyl tartrate in *s*-tetrachloroethane were compared (p. 1148). In the table below

	iso*Butyl Tartrate in* s-*Tetrachloroethane.*				iso*Butyl Diacetyltartrate in* o-*Nitrotoluene.*			
Blue cuts.	$p = 33{\cdot}362$		$p = 48{\cdot}15$		$p = 24{\cdot}964$		$p = 58{\cdot}86$	
	[M]	*t.*	[M]	*t.*	[M]	*t.*	[M]	*t.*
g	+26·3°	+21·5°	+28·5°	+16·0°	+30·1°	+147°	+33·0°	+104·0°
y	23·7	17·5	24·7*	10·0	29·3	145	29·6	95·4
r_2 ...	19·6	11·0	18·7*	1·5	26·0	137	27·0	89·0
r_1 ...	16·4	6·5	14·0*	−6·0	25·3	135	22·8	78·5

* Extrapolated.

are shown the values of the rotations at the intersections of the blue lines with the other four lines examined. In the case of *o*-nitrotoluene the points of intersection unfortunately cannot be given for the violet line, since this is difficult to read on account of the colour of the solutions. In addition to this, for the more concentrated solution of *iso*butyl tartrate in *s*-tetrachloroethane the points of intersection for the blue line have to be obtained by extrapolation, and are, therefore, of course, not quite so accurate as the others.

It is clear, however, that for each active substance in its two solutions in one solvent the intersections take place at very nearly the same rotation values, but at different temperatures, and further, that the rotation values of the intersections in the case of *iso*butyl diacetyltartrate are very nearly the same as the values for the corresponding intersections in the case of the simple ester. Thus for the more dilute solution in each case blue cuts green for *iso*butyl tartrate in *s*-tetrachloroethane at a molecular rotation of 26·3°, whereas for the diacetyl ester in *o*-nitrotoluene the intersection occurs at a rotation of 30·1°, the other values being respectively 23·7° and 29·3°; 19·6° and 26°; 16·4° and 25·3°.

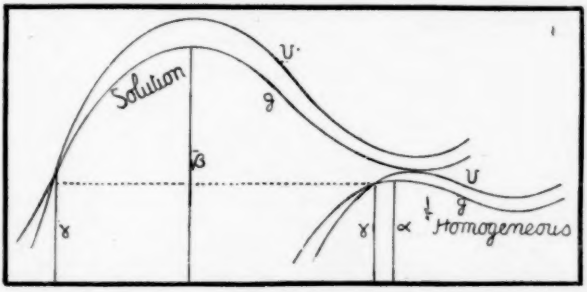
It must be admitted that this agreement is very striking indeed. The numbers do not agree exactly, and they probably ought not to do so, but they appear to reveal a very fundamental similarity between the rotational behaviour of these two esters.

It thus seems clear that by means of an examination of the rotation of homogeneous ethyl tartrate, of homogeneous *iso*butyl tartrate, of these esters in *s*-tetrachloroethane and in quinoline, and of *iso*butyl diacetyltartrate in the homogeneous state and also in solution in quinoline, in *s*-tetrachloroethane, and in *o*-nitrotoluene, we are able to arrive at a satisfactory qualitative idea of what would be the behaviour of all three esters on heating from a low temperature to a high temperature. We learn that all the temperature–rotation graphs would show visibly anomalous rotation-dispersion at one particular region and at fairly similar rotation values; that beyond this region, at higher temperatures, a maximum is reached, after which the curves tend, but without any further intersection, towards a new minimum at which the rotation values are positive and not high; that at this minimum the curves run parallel, and after passing it they rise, again without intersection, to some new maximum which has not yet been explored. In this way there may be obtained, for the first time, some real notion as to how the rotatory powers of related active compounds are connected with each other.

Further, it is now possible to form an opinion as to the influ-

ence of a solvent on the rotation of an active substance. This will be clearest from Fig. 6, which represents, in a rough and purely qualitative fashion, the influence of quinoline on the esters mentioned above. On solution the temperature–rotation curves for the homogeneous ester are shifted as a whole towards a much lower temperature in the cases of ethyl tartrate and of *iso*butyl tartrate, but are not much shifted in the case of *iso*butyl diacetyltartrate. In all three cases, however, the curves in the region of the maximum are much more opened out in this solvent, although perhaps, if calculated from a rational zero,* the dispersion may remain approximately constant. It appears also, and is probably the most

FIG. 6.



interesting point of all, that although the rotation value at the maximum is very different in solution and in the homogeneous condition, the rotation value at the intersection of any two given curves is either the same or very nearly so.

These views suggest very clearly at least some directions in which future work must be undertaken; they seem to be wholly in agreement with recent comprehensive research on the subject, such as that of Pickard and Kenyon, and if they should appear to lack anything of what is often popularly regarded as explanation, the deficiency will doubtless be excused by those who recognise the truth of the statement that "all science is description and not explanation." †

* See following paper.

† K. Pearson, "Grammar of Science," 3rd ed., p. viii.

Experimental Data.

Homogeneous Ethyl Tartrate. M = 206.

Sample carefully distilled; b. p. 137°/5 mm.; bath, 165°.

Densities:

t	−23·0°	0·0°	15·5°	38·55°	59·4°
d	1·2484	1·2254	1·2097	1·1865	1·1656
t	96·0°	115·6°	159·5°	193·0°	223·5°
d	1·1287	1·1088	1·0646	1·0308	1·0003

λ = 6980:

t	−20·0°	0·0°	15·5°	38·55°	59·4°	96·25°
α (100 mm.)	+ 3·737	6·21	7·73	9·509	10·627	11·833
$[\alpha]$	3·00	5·07	6·39	8·01	9·12	10·49
[M]	6·18	10·44	13·16	16·51	18·78	21·60
t	114·9°	133·3°	159·1°	194·2°	223·5°	
α (100 mm.)	12·133	12·332	12·338	11·962	11·581	
$[\alpha]$	10·93	11·30	11·58	11·62	11·58	
[M]	22·52	23·29	23·86	23·93	23·85	

λ = 6708:

t	−21·0°	0·0°	15·5°	38·55°	59·4°	96·0°
α (100 mm.)	+ 3·77	6·337	8·035	9·905	11·155	12·477
$[\alpha]$	3·02	5·17	6·64	8·35	9·57	11·05
[M]	6·23	10·65	13·68	17·19	19·71	22·77
t	115·1°	133·4°	159·5°	192·5°	223·5°	
α (100 mm.)	12·775	12·951	12·893	12·665	12·071	
$[\alpha]$	11·51	11·87	12·11	12·28	12·07	
[M]	23·72	24·46	24·95	25·3	24·86	

λ = 6450:

t	−23·0°	0·0°	15·5°	38·6°	59·7°	95·7°
α (100 mm.)	+3·25	6·551	8·277	10·332	11·688	13·106
$[\alpha]$	2·60	5·35	6·84	8·71	10·032	11·61
[M]	5·36	11·01	14·09	17·94	20·655	23·91
t	114·7°	133·7°	158·8°	193·2°	223·5°	
α (100 mm.)	13·495	13·643	13·655	13·343	12·755	
$[\alpha]$	12·16	12·51	12·82	12·95	12·75	
[M]	25·05	25·77	26·40	26·67	26·27	

λ = 6232:

t	−25·0°	0·0°	15·5°	38·6°	59·8°
α (100 mm.)	2·588	6·638	8·50	10·72	12·195
$[\alpha]$	2·07	5·42	7·03	9·04	10·47
[M]	4·26	11·16	14·47	18·61	21·56
t	115·6°	133·3°	159·8°	193·0°	223·5°
α (100 mm.)	14·195	14·36	14·42	14·065	13·455
$[\alpha]$	12·80	13·07	13·55	13·64	13·45
[M]	26·37	26·92	27·90	28·11	27·71

Homogeneous Ethyl Tartrate (continued).

$\lambda = 5769$:

t	−22·0°	0·0°	15·6°	16·1°	38·6°	59·6°
a (100 mm.)	2·322	6·562	8·863	8·94	11·567	13·45
$[a]$	1·86	5·35	7·33	7·39	9·75	11·74
[M]	3·84	11·03	15·09	15·23	20·08	23·77

t	93·7°	114·9°	133·3°	159·3°	190·0°	223·5°
a (100 mm.)	15·348	15·942	16·208	16·35	16·053	15·417
$[a]$	13·57	14·37	14·86	15·35	15·53	15·41
[M]	27·96	29·60	30·60	31·63	31·99	31·75

$\lambda = 5460{\cdot}7$:

t	−25·5°	0·0°	14·1°	15·6°	16·1°	38·6°	59·5°
a (100 mm.)	+1·555	6·113	8·5	8·785	8·85	11·907	14·055
$[a]$	1·24	4·99	7·02	7·26	7·32	10·04	12·06
[M]	2·56	10·27	14·46	14·96	15·07	20·73	24·84

t	94·0°	114·6°	133·3°	158·5°	190·0°	223·5°
a (100 mm.)	16·328	17·063	17·403	17·622	17·375	16·711
$[a]$	14·44	15·37	15·96	16·54	16·81	16·71
[M]	29·75	31·67	32·87	34·07	34·62	34·42

$\lambda = 4959{\cdot}7$:

t	−27·0°	−23·0°	−20·0°	0·0°	15·5°	38·6°	59·8°
a (100 mm.)	−3·27	−2·315	−0·948	+4·062	7·476	11·606	14·395
$[a]$	−2·61	−1·85	−0·76	+3·31	6·18	9·78	12·35
[M]	−5·38	−3·82	−1·57	+6·83	12·73	20·15	25·45

t	94·9°	115·0°	133·3°	159·1°	194·0°	223·5°
a (100 mm.)	17·62	18·61	19·23	19·65	19·586	18·809
$[a]$	15·60	16·77	17·63	18·45	19·02	18·80
[M]	32·13	34·55	36·32	38·01	39·18	38·73

$\lambda = 4358$:

t	−24·5°	0·0°	16·1°	38·6°	59·6°	94·5°
a (100 mm.)	−13·51	−3·798	+1·362	7·287	11·592	16·53
$[a]$	−10·81	−3·10	+1·13	6·14	9·95	14·63
[M]	−22·27	−6·38	+2·32	12·65	20·49	30·13

t	114·9°	133·3°	159·8°	191·6°	223·5°
a (100 mm.)	18·265	19·44	20·528	21·083	20·817
$[a]$	16·46	17·82	19·28	20·43	20·81
[M]	33·91	36·71	39·73	42·08	42·87

iso*Butyl Tartrate*. M = 262.

The ester boiled at 178°/8 mm.; bath, 230°.

Density determined:

t	182°	
d	0·9317.	This was taken in conjunction with previous determinations (T., 1913, **103**, 174·5, where the value at 108·6° should be 1·0007, not 1·0075).

iso*Butyl Tartrate* (continued).

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	d.	$[\alpha]$	[M].
73·0°	+16·379	1·0325	15·863	41·56
99·05	16·483	1·0094	16·328	42·78
132·0	16·073	0·9788	16·422	43·03
171·7	15·083	0·9416	16·016	41·96
193·0	14·407	0·9212	15·640	40·98
226·3	13·583	0·8892	15·275	40·02

r_2, $\lambda = 6234{\cdot}3$:

73·0°	18·517	1·0325	17·936	46·99
99·05	18·686	1·0094	18·510	48·50
132·0	18·331	0·9788	18·729	49·07
171·7	17·237	0·9416	18·305	47·96
193·0	16·516	0·9212	17·930	46·98
226·3	15·383	0·8892	17·302	45·33

y, $\lambda = 5790{\cdot}5$:

73·0°	21·166	1·0325	20·50	53·71
99·05	21·366	1·0094	21·166	55·45
132·0	20·971	0·9788	21·426	56·13
171·7	19·716	0·9416	20·937	54·86
193·0	18·936	0·9212	20·557	53·86
226·3	17·597	0·8892	19·793	51·86

g, $\lambda = 5460{\cdot}7$:

73·0°	23·510	1·0325	22·769	59·66
99·05	23·558	1·0094	23·337	61·15
132·0	23·140	0·9788	23·643	61·95
171·7	21·789	0·9416	23·139	60·62
193·0	20·918	0·9212	22·71	59·50
226·3	19·535	0·8892	21·97	57·56

b, $\lambda = 4959{\cdot}7$:

73·0°	26·987	1·0325	26·143	68·5
99·05	27·450	1·0094	27·194	71·25
132·0	27·166	0·9788	27·752	72·71
171·7	25·740	0·9416	27·336	71·62
193·0	24·74	0·9212	26·856	70·36
226·3	23·145	0·8892	26·032	68·20

v, $\lambda = 4358{\cdot}3$:

73·0°	30·651	1·0325	29·687	77·78
99·05	31·693	1·0094	31·397	82·26
132·0	31·643	0·9788	32·330	84·71
171·7	30·230	0·9416	32·104	84·11
193·0	29·227	0·9212	31·73	83·13
226·3	27·524	0·8892	30·957	81·11

iso*Butyl Tartrate in* s-*Tetrachloroethane.*

$p = 33{\cdot}362$:

Densities:

t ...	0·0°	16·2°*	16·4°	43·96°*	44·0°	68·0°	99·4°	99·7° *
d ...	1·4035	1·3833	1·3831	1·3482	1·3481	1·3179	1·2782	1·2778

* Experimental.

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	$[\alpha]$	[M]
0·0°	2·556	5·459	14·30
16·4	3·447	7·471	19·57
44·0	4·582	10·188	26·69
68·0	5·232	11·90	31·18
99·4	5·655	13·26	34·74

r_2, $\lambda = 6234{\cdot}3$:

0·0°	2·723	5·816	15·23
16·4	3·797	8·229	21·56
44·0	5·122	11·389	29·84
68·0	5·867	13·343	34·96
99·4	6·36	14·915	39·08

y, $\lambda = 5790{\cdot}5$:

0·0°	2·797	5·974	15·65
16·4	4·100	8·886	23·28
44·0	5·659	12·583	32·97
68·0	6·555	14·908	39·06
99·4	7·183	16·844	44·13

g, $\lambda = 5460{\cdot}7$:

0·0°	2·722	5·813	15·23
16·4	4·220	9·146	23·96
44·0	6·039	13·428	35·18
68·0	7·045	16·013	41·96
99·4	7·827	18·353	48·09

b, $\lambda = 4959{\cdot}7$:

0·0°	2·132	4·553	11·93
16·4	4·079	8·84	23·16
44·0	6·440	14·320	37·52
68·0	7·852	17·838	46·74
99·4	8·862	20·78	54·44

v, $\lambda = 4358{\cdot}3$:

0·0°	−0·122	−0·261	−0·683
16·4	+2·597	+5·628	+14·74
44·0	5·988	13·314	34·88
68·0	8·018	18·235	47·78
99·4	9·619	22·558	59·10

$p = 48{\cdot}15$:

Densities determined:

t	24·8°	30·2°*	42·2°	50·8°*	67·0°	72·8°*	99·65°*
d	1·2927	1·2867	1·2729	1·2630	1·2442	1·2377	1·2061

* Experimental.

iso*Butyl Tartrate in* s-*Tetrachloroethane* (continued).

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	[α]	[M]
24·8°	+5·782	+9·289	+24·34
42·2	6·647	10·846	28·42
67·0	7·422	12·390	32·46
99·65	8·000	13·776	36·09

r_2, $\lambda = 6234{\cdot}3$:

24·8°	6·500	10·443	27·36
42·2	7·500	12·236	32·06
67·0	8·427	14·067	36·86
99·65	9·055	15·592	40·85

y, $\lambda = 5790{\cdot}5$:

24·8°	7·156	11·497	30·12
42·2	8·325	13·583	35·59
67·0	9·477	15·820	41·45
99·65	10·225	17·607	46·13

g, $\lambda = 5460{\cdot}7$:

24·8°	7·593	12·20	31·96
42·2	8·928	14·566	38·16
67·0	10·310	17·211	45·09
99·65	11·198	19·283	50·52

b, $\lambda = 4959{\cdot}7$:

24·8°	7·932	12·743	33·39
42·2	9·704	15·832	41·48
67·0	11·531	19·249	50·43
99·65	12·809	22·057	57·79

v, $\lambda = 4358{\cdot}3$:

24·8°	6·872	11·040	28·925
42·2	9·378	15·300	40·09
67·0	12·026	20·075	52·60
99·65	14·090	24·263	63·570

Ethyl Tartrate in Salicylaldehyde. B. p. 77°/12 mm.; bath, 108°.

$p = 20{\cdot}214$:

Densities determined:

t	18·5°	43·0°	71·3°	100·0°
d	1·1752	1·1516	1·1234	1·0948

$\lambda = 6907{\cdot}5$:

t.	α (100 mm.)	*d.*	[α]	[M]
19·8°	4·827	1·1743	20·33	41·88
32·1	4·705	1·1620	20·027	41·26
61·1	4·539	1·1335	19·81	40·81
79·45	4·312	1·1155	19·136	39·42
114·2	3·981	1·0805	18·228	37·55

Ethyl Tartrate in Salicylaldehyde (continued).

r_2, λ = 6234·4:

t.	α (100 mm.)	*d.*	[α]	[M]
19·7°	5·667	1·1744	23·87	49·17
32·2	5·519	1·1619	23·496	48·40
61·1	5·263	1·1335	22·97	47·32
79·5	5·042	1·1155	22·36	45·80
114·2	4·635	1·0805	21·223	43·72

y, λ = 5790·5:

19·2°	6·499	1·1747	27·37	56·37
33·7	6·315	1·1605	26·917	55·45
60·9	6·012	1·1339	26·23	54·04
79·5	5·762	1·1155	25·554	52·64
114·2	5·287	1·0805	24·21	49·87

g, λ = 5460·7:

19·0°	7·217	1·1749	30·387	62·60
34·2	7·019	1·1601	29·93	61·65
61·45	6·672	1·1333	29·123	59·99
79·5	6·389	1·1155	28·32	58·33
114·2	5·840	1·0805	26·74	55·08

b, λ = 4959·7:

19·55°	8·484	1·1745	35·73	73·61
32·7	8·270	1·1614	35·22	72·56
61·1	7·888	1·1335	34·425	70·92
79·5	7·507	1·1155	33·29	68·58
114·2	6·902	1·0805	31·57	65·02

v, λ = 4358·3:

19·4°	10·332	1·1746	43·52	89·64
33·9	9·948	1·1608	42·39	87·32
61·1	9·377	1·1335	40·93	84·31
79·5	8·971	1·1155	39·34	81·04
114·2	8·101	1·0805	37·094	76·4

Ethyl Tartrate in Benzaldehyde.

Densities:

t ...	13·84°*	16·5°	17·0°	48·0°*	85·5°	86·2°	86·7°	92·8°*	135·5°
d ...	1·0756	1·0735	1·0730	1·0446	1·0087	1·0079	1·0075	1·0020	0·9603

* Experimental.

	λ = 6232:			λ = 5769:		
t	17·0°	86·7°	135·5°	17·0°	85·5°	135·5°
α (100 mm.) ...	+4·055	2·765	2·256	4·710	3·210	2·639
[α]	39·12	26·49	22·66	42·35	30·71	26·52
[M]	80·59	54·57	46·68	87·24	63·26	54·63

g, λ = 5460·7:

t	11·7°	17·0°	86·7°	135·5°
α (100 mm.) ...	5·442	5·263	3·543	2·904
[α]	48·73	47·33	33·93	29·18
[M]	100·4	97·49	69·89	60·12

Ethyl Tartrate in Benzaldehyde (continued).

	b, λ=4959·7:			*v*, λ=4358·3:		
t	17·0°	86·2°	135·5°	16·5°	85·5°	135·5°
a (100 mm.) ...	6·367	4·175	3·391	8·18	5·147	4·173
[*a*]	57·26	39·96	34·07	73·51	49·66	41·93
[M]	117·9	82·33	70·19	151·4	102·26	86·38

Ethyl Tartrate in Quinoline.

p=4·972.

Densities:

t	14·3°*	19·8°	49·8°*	60·5°	82·0°	96·0°*
d	1·1049	1·1000	1·0766	1·0674	1·0494	1·0379

* Experimental.

λ=6708 (Li):

t	19·8°	60·85°	82·0°	99·0°
a (100 mm.) ...	1·509	1·059	0·946	0·899
[*a*]	38·25	19·96	18·13	17·47
[M]	78·80	41·12	37·35	35·99
d	1·1000	1·0670	1·0494	1·0349

r_2, λ=6234·3:

t	19·8°	60·75°	82·0°	99·0°
a (100 mm.) ...	1·657	1·185	1·073	1·003
[*a*]	30·30	22·33	20·57	19·5
[M]	62·41	46·01	42·36	40·16
d	1·1000	1·0671	1·0494	1·0349

y, λ=5790·5:

t	19·8°	60·3°	82·0°	99·0°
a (100 mm.) ...	1·918	1·377	1·226	1·150
[*a*]	35·07	25·94	23·50	22·35
[M]	72·24	53·43	48·40	46·05
d	1·1000	1·0677	1·0494	1·0349

g, λ=5460·7:

t	19·8°	60·3°	82·0°	99·0°
a (100 mm.) ...	2·092	1·472	1·312	1·239
[*a*]	38·25	27·73	25·15	24·08
[M]	78·80	57·13	51·80	49·61
d	1·1000	1·0677	1·0494	1·0349

b, λ=4959·7:

t	19·8°	60·5°	82·0°	99·0°
a (100 mm.) ...	2·406	1·651	1·448	1·403
[*a*]	44·00	31·11	27·75	27·27
[M]	90·62	64·08	57·17	56·18
d	1·1000	1·0674	1·0494	1·0369

v, λ=4358·3:

t	19·8°	59·9°	82·0°	99·0°
a (100 mm.) ...	2·705	1·720	1·631	1·502
[*a*]	49·46	32·39	31·26	29·20
[M]	101·9	66·73	64·39	60·13
d	1·1000	1·0679	1·0494	1·0349

Ethyl Tartrate in Quinoline (continued).

$p = 13{\cdot}601$.

Densities:

t	−13·0°	0·0°	16·5°*	16·82°	39·1°*	44·5°	60·6°*	65·1°	116·0°
d	1·1393	1·1291	1·1154	1·1151	1·0966	1·0920	1·0786	1·0748	1·0330

* Experimental.

$\lambda = 6708$ (Li):

t	−13·0°	0·0°	44·5°	65·1°	116·0°
α (100 mm.)	5·369	4·780	3·208	2·805	2·558
$[\alpha]$	34·65	31·13	31·60	19·19	18·21
[M]	71·39	64·12	44·50	39·53	37·51

r_2, $\lambda = 6234{\cdot}3$:

t	−13·0°	0·0°	16·82°	44·5°	65·1°	116·0°
α (100 mm.)	6·091	5·409	4·593	3·645	3·150	2·860
$[\alpha]$	39·32	35·23	30·29	24·54	21·55	20·36
[M]	80·99	72·56	62·39	50·55	44·39	41·94

y, $\lambda = 5790{\cdot}5$:

t	−11·5°	0·0°	16·82°	44·5°	65·1°	116·0°
α (100 mm.)	7·09	6·326	5·346	4·157	3·579	3·220
$[\alpha]$	45·81	41·20	35·26	28·00	24·48	22·92
[M]	94·46	84·90	72·62	57·67	50·43	47·22

g, $\lambda = 5460{\cdot}7$:

t	−12·0°	0·0°	16·82°	44·5°	65·1°	116·0°
α (100 mm.)	7·884	6·973	5·867	4·544	3·912	3·532
$[\alpha]$	50·93	45·42	38·70	30·60	26·76	25·14
[M]	104·9	93·56	79·70	63·03	55·13	51·79

b, $\lambda = 4959{\cdot}7$:

t	−12·0°	0·0°	16·82°	44·5°	65·1°
α (100 mm.)	9·42	8·255	6·850	5·222	4·446
$[\alpha]$	60·86	53·77	45·18	35·17	30·41
[M]	125·3	110·8	93·08	72·44	62·65

v, $\lambda = 4358{\cdot}3$:

t	−11·5°	0·0°	16·82°	44·5°	65·1°
α (100 mm.)	11·289	9·769	7·894	5·758	4·762
$[\alpha]$	72·94	63·63	52·06	38·78	32·58
[M]	150·3	131·1	107·2	79·88	67·11

Ethyl Tartrate in Pyridine.

$p = 19{\cdot}263$.

t	0·0°	13·8°*	15·7°	43·6°*	58·6°	66·3°*	91·6°*	100·0°
d	1·0410	1·0277	1·0262	0·9981	0·9878	0·9742	0·9476	0·9386

* Experimental.

Li_r, $\lambda = 6708$:

t.	α (100 mm.)	$[\alpha]$	[M]
0·0°	+6·965	34·74	71·56
15·7	6·376	32·26	66·45
58·6	5·020	26·38	54·35
100·0	3·975	21·99	45·29

Ethyl Tartrate in Pyridine (continued).

r_2, $\lambda = 6234{\cdot}3$:

t.	α (100 mm.)	[α].	[M].
0·0°	7·921	39·50	81·37
15·7	7·240	36·63	75·46
58·6	5·689	29·90	61·60
100·0	4·553	25·185	51·88

Hg_y, $\lambda = 5769$:

0·0°	9·374	46·75	96·29
15·7	8·544	43·23	89·04
58·6	6·664	35·03	72·15
100·0	5·333	29·50	60·77

g, $\lambda = 5460{\cdot}7$:

0·0°	10·437	52·06	107·22
15·7	9·508	48·11	99·10
58·6	7·364	38·704	79·72
100·0	5·899	32·63	67·21

b, $\lambda = 4959{\cdot}7$:

0·0°	12·530	62·48	128·7
15·7	11·390	57·63	118·71
58·6	8·730	45·89	94·52
100·0	6·944	38·41	79·12

v, $\lambda = 4358{\cdot}3$:

0·0°	15·768	78·63	161·97
15·7	14·242	72·06	148·44
58·6	10·824	59·90	117·2
100·0	8·408	46·51	95·80

iso*Butyl Tartrate in Quinoline.*

$p = 20{\cdot}066$.

Densities determined:

t	18·0°	38·95°	69·55°	99·55°	151·0°
d	1·1003	1·0832	1·0580	1·0330	0·9880

50 mm. tube used.

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	d.	[α]	[M]
0·0°	+12·192	1·1150	54·49	142·76
39·35	8·56	1·0828	39·40	103·2
69·75	6·934	1·0577	32·67	85·6
99·5	5·876	1·0332	28·35	74·28
147·5	4·680	0·9912	23·53	61·65

r_2, $\lambda = 6234{\cdot}3$:

0·0°	14·16	1·1150	63·29	165·81
39·35	9·914	1·0828	45·63	119·6
69·75	8·000	1·0577	37·69	98·75
99·5	6·734	1·0332	32·48	85·1
147·5	5·628	0·9912	28·30	74·14

iso*Butyl Tartrate in Quinoline* (continued).

y, λ=5790·5:

t.	*a*(100 mm.)	*d.*	[*a*]	[M]
0·0°	16·494	1·1150	73·72	193·12
18·0	13·810	1·1003	62·56	163·9
39·35	11·470	1·0828	52·79	138·3
69·75	9·124	1·0577	42·99	112·6
99·5	7·720	1·0332	37·24	97·57
144·2	6·614	0·9942	33·16	86·86

g, λ=5460·7:

0·0°	18·650	1·1150	83·36	218·4
39·35	12·916	1·0828	59·45	155·8
69·75	10·220	1·0577	48·15	126·2
99·5	8·680	1·0332	41·87	109·7
145·0	7·308	0·9935	36·66	96·04

b, λ=4959·7:

0·0°	23·142	1·1150	103·44	271·0
39·35	15·752	1·0828	72·50	189·9
69·75	12·442	1·0577	58·62	153·6
99·5	10·492	1·0332	50·61	132·6
147·5	8·542	0·9912	42·94	112·5

v, λ=4358·3:

0·0°	29·878	1·1150	133·63	350·1
39·35	19·874	1·0828	91·47	239·6
69·75	15·550	1·0577	73·26	191·9
99·5	12·910	1·0332	62·28	163·2
146·0	10·474	0·9926	52·59	137·8

iso*Butyl Diacetyl*-d-*tartrate*. M=346.

The ester boiled at 157°/3·5 mm.; bath, 190°. Rotation determined in a 50 mm. tube.

t	−21·0°	−20·0°	−19·0°	−18·7°	−18·0°	0·0°
d	1·1218	1·1209	1·1200	1·1198	1·1192	1·1024
t	13·7°*	14·0°	17·25°	41·8°*	42·25°	69·96°*
d	1·0898	1·0895	1·0864	1·0637	1·0633	1·0368
t	75·2°	99·3°*	98·9°	200·0°	202·0°*	
d	1·0327	1·0093	1·0105	0·9087	0·9066	

* Experimental.

λ=6742:

t.	*a* (100 mm.)	[*a*]	[M]
−18·0°	16·018	14·314	49·53
0·0	14·916	13·53	46·81
+14·0	14·012	12·86	44·51
17·25	13·933	12·826	44·38
42·25	12·988	12·214	42·26
75·2	12·304	11·915	41·23
98·9	12·070	11·944	41·33
200·0	12·976	14·281	49·41

iso*Butyl Diacetyl*-d-*tartrate* (continued).

r_2, $\lambda = 6234{\cdot}3$:

t.	α (100 mm.)	[α]	[M]
−18·7°	18·300	16·342	56·54
0·0	16·860	15·293	52·91
+14·0	16·006	14·69	50·83
17·25	15·800	14·544	50·32
42·25	14·818	13·936	48·22
75·2	14·052	13·607	47·08
98·9	13·946	13·800	47·75
200·0	14·997	16·506	57·11

y, $\lambda = 5790{\cdot}5$:

−21·0°	20·896	18·626	64·45
0·0	19·112	17·336	59·98
+14·0	18·066	16·580	57·37
17·25	17·833	16·417	56·80
42·25	16·748	15·752	54·50
75·2	15·952	15·446	53·44
98·9	15·850	15·685	54·27
200·0	17·267	19·002	65·75

g, $\lambda = 5460{\cdot}7$:

−21·0°	22·814	20·334	70·36
0·0	20·890	18·948	65·56
+14·0	19·780	18·15	62·82
17·25	19·517	17·958	62·13
42·25	18·284	17·094	59·49
75·2	17·488	16·935	58·60
98·9	17·484	17·302	59·86
200·0	19·319	21·26	73·56

b, $\lambda = 4959{\cdot}7$:

−19·0°	25·966	23·18	80·21
0·0	23·848	21·63	74·84
+14·0	22·592	20·74	71·75
42·25	20·994	19·745	68·32
75·2	20·236	19·596	67·80
98·9	20·348	20·135	69·67

v, $\lambda = 4358{\cdot}3$:

−20·0°	28·936	25·816	89·32
0·0	26·298	23·855	82·54
+14·0	24·970	22·92	79·30
42·25	23·314	21·926	75·86
75·2	22·944	22·218	76·88
98·9	23·566	23·318	80·69
200·0	28·580	31·45	108·82

iso*Butyl Diacetyl*-d-*tartrate in Quinoline.*

$p = 20{\cdot}476$.

Densities observed:

t	15·55°	36·78°	65·11°	100·0°
d	1·0970	1·0794	1·0561	1·0280

Note that this density graph curves the opposite way to what is customary.

iso*Butyl Diacetyl*-d-*tartrate in Quinoline* (continued).

Hg_r, $\lambda = 6907{\cdot}5$:

t.	α (100 mm.)	*d.*	[α]	[M]
17·1°	+6·369	1·0957	+28·39	98·23
36·95	5·554	1·0792	25·135	86·97

$\lambda = 6742$:

0·0°	7·619	1·1098	33·53	116·0
76·78	4·581	1·0467	21·374	74·96
103·25	4·092	1·0253	19·492	67·45

r_2, $\lambda = 6234{\cdot}3$:

0·0°	8·935	1·1098	39·32	136·05
17·0	7·706	1·0957	34·35	118·85
36·7	6·617	1·0794	29·94	103·4
76·75	5·222	1·0467	24·365	84·30
103·1	4·644	1·0253	22·122	76·54
126·0	4·252	1·0069	20·624	71·36

y, $\lambda = 5790{\cdot}5$:

0·0°	10·561	1·1098	46·48	160·8
16·8	9·095	1·0959	40·53	140·24
38·4	7·720	1·0780	34·974	121·02
76·9	6·120	1·0466	28·558	98·82
103·4	5·404	1·0253	25·742	89·07
126·0	5·011	1·0069	24·305	84·10

g, $\lambda = 5460{\cdot}7$:

0·0°	11·997	1·1098	52·79	182·7
16·8	10·335	1·0959	46·15	159·68
38·63	8·735	1·0778	39·58	136·96
76·62	6·909	1·0468	32·233	111·54
103·4	6·124	1·0253	29·172	100·93

b, $\lambda = 4959{\cdot}7$:

0·0°	14·830	1·1098	65·26	226·16
16·95	12·882	1·0958	57·41	198·65
36·55	10·969	1·0796	49·62	171·7
76·75	8·406	1·0467	39·222	135·7
103·2	7·422	1·0253	35·354	122·32

v, $\lambda = 4358{\cdot}3$:

0·0°	20·345	1·1098	89·54	309·8
16·9	17·203	1·0958	76·67	265·3
38·85	14·337	1·0776	64·99	224·85
76·73	10·929	1·0467	50·995	176·42

Not readable at higher temperatures.

$p = 74{\cdot}96$.

Densities observed:

t	16·5°	41·35°	61·3°	99·6°
d	1·0927	1·0703	1·0524	1·0177

iso*Butyl Diacetyl*-d-*tartrate in Quinoline* (continued).

$\lambda = 6742$:

t.	α (100 mm.).	*d*.	[α]	[M]
0·0°	12·880	1·1076	15·514	53·68
16·6	11·989	1·0926	14·639	50·65
59·75	10·449	1·0538	13·227	45·77
100·0	9·832	1·0177	12·886	45·59

r_g, $= 6234{\cdot}3$:

0·0°	14·788	1·1076	17·813	61·64
16·6	13·700	1·0926	16·728	57·88
59·75	11·968	1·0538	15·15	52·42
100·0	11·270	1·0177	14·772	51·11

y, $\lambda = 5790{\cdot}5$:

0·0°	16·870	1·1076	20·32	70·31
16·2	15·703	1·0930	19·166	66·32
59·75	13·637	1·0538	17·264	59·73

g, $\lambda = 5460{\cdot}7$:

0·0°	18·632	1·1076	22·442	77·65
16·2	17·280	1·0930	21·09	72·98
59·75	15·060	1·0538	19·064	65·96
100·0	14·307	1·0177	18·754	64·89

b, $\lambda = 4959{\cdot}7$:

0·0°	21·765	1·1076	26·217	90·72
16·4	20·109	1·0928	24·55	84·94
59·75	17·550	1·0538	22·217	76·88
100·0	16·796	1·0177	22·016	76·17

v, $\lambda = 4358{\cdot}3$:

0·0°	25·355	1·1076	30·54	105·67
16·4	23·464	1·0928	28·648	99·12
59·75	20·300	1·0538	25·70	88·93
100·0	Unreadable.			

It is very noticeable that quinoline and this ester only mix very sluggishly, which is not what one would expect if solution were a form of chemical combination. On the other hand, the solvent influence is very great.

iso*Butyl Diacetyl*-d-*tartrate* (b. p. 183°/8 mm.) *in* s-*Tetrachloroethane.*

$p = 20{\cdot}034$.

Densities determined:

t	16·03°	43·0°	75·8°	99·75°
d.....	1·4670	1·4304	1·3854	1·3519

iso*Butyl Diacetyl*-d-*tartrate in* s-*Tetrachloroethane* (continued).

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	*d.*	[α]	[M]
0·0°	+3·166	1·4887	10·616	36·73
17·05	2·924	1·4657	9·859	34·11
43·0	2·720	1·4304	9·492	32·84
57·3	2·679	1·4107	9·479	32·80
76·85	2·592	1·3840	9·349	32·35
99·75	2·607	1·3519	9·626	33·31

r_2, $\lambda = 6234{\cdot}3$:

0·0°	3·505	1·4887	11·752	40·66
16·9	3·262	1·4658	11·106	38·43
43·0	3·030	1·4304	10·574	36·59
57·5	2·964	1·4107	10·487	36·29
76·85	2·884	1·3840	10·403	35·99
99·75	2·925	1·3519	10·802	37·38

y, $\lambda = 5790{\cdot}5$:

0·0°	3·895	1·4887	13·06	45·19
16·2	3·680	1·4669	12·522	43·33
43·0	3·400	1·4304	11·866	41·06
56·5	3·287	1·4120	11·618	40·20
76·85	3·245	1·3840	11·703	40·49
99·75	3·282	1·3519	12·119	41·93

g, $\lambda = 5460{\cdot}7$:

0·0°	4·250	1·4887	14·25	49·31
16·2	3·962	1·4669	13·481	46·65
43·0	3·672	1·4304	12·815	44·34
57·5	3·584	1·4107	12·680	43·88
76·85	3·530	1·3840	12·732	44·05
99·75	3·585	1·3519	13·238	45·81

b, $\lambda = 4959{\cdot}7$:

0·0°	4·732	1·4887	15·866	54·89
16·9	4·384	1·4658	14·93	51·66
43·0	4·095	1·4304	14·292	49·45
57·5	4·030	1·4107	14·262	49·34
76·85	3·994	1·3840	14·406	49·84
99·75	4·136	1·3519	15·272	52·84

v, $\lambda = 4358{\cdot}3$:

0·0°	4·924	1·4887	16·51	57·12
16·5	4·542	1·4664	15·46	53·49
43·0	4·199	1·4304	14·654	50·71
58·3	4·184	1·4095	14·806	51·27
76·85	4·295	1·3840	15·491	53·60
99·75	4·544	1·3519	16·78	58·06

iso*Butyl Diacetyl*-d-*tartrate in* o-*Nitrotoluene.*

$p = 24{\cdot}694$.

The *o*-nitrotoluene was distilled under diminished pressure, then partly frozen, the liquid drained off, and the residue redistilled. B. p. 99°/9 mm.

Densities determined:

t	16·6°	43·2°	70·05°	99·7°
d	1·1454	1·1200	1·0945	1·0657

r_1, $\lambda = 6716{\cdot}3$:

t.	α (100 mm.)	d.	[α]	[M]
0·0°	−0·884	1·1614	−3·082	−10·66
17·4	−0·380	1·1448	−1·344	−4·65
49·8	+0·452	1·1088	+1·6514	+5·71
73·7	+1·006	1·0908	+3·735	+12·99
150·0	+1·930	1·0176	+7·681	+26·57

r_2, $\lambda = 6234{\cdot}3$:

0·0°	−1·320	1·1614	−4·602	−15·92
17·4	−0·790	1·1448	−2·795	−9·67
49·8	+0·194	1·1088	+0·709	+2·45
73·7	+0·804	1·0908	+2·985	+10·33
150·0	+2·087	1·0176	+8·306	+28·74

y, $\lambda = 5790{\cdot}5$:

0·0°	−2·064	1·1614	−7·196	−24·90
17·0	−1·368	1·1451	−4·838	−16·74
49·8	−0·134	1·1088	−0·489	−1·69
73·7	+0·666	1·0908	+2·473	+8·56
150·0	+2·220	1·0176	+8·835	+30·57

g, $\lambda = 5460{\cdot}7$:

0·0°	−2·924	1·1614	−10·194	−35·28
17·0	−2·080	1·1451	−7·356	−25·45
49·8	−0·532	1·1088	−1·943	−6·72
73·7	+0·436	1·0908	+1·619	+5·60
150·0	+2·262	1·0176	+9·002	+31·15

b, $\lambda = 4959{\cdot}7$:

0·0°	−5·566	1·1614	−19·406	−67·15
17·4	−4·170	1·1448	−14·75	−51·04
49·8	−1·954	1·1088	−7·137	−24·69
73·7	−0·520	1·0908	−1·93	−6·68
150·0	+2·290	1·0176	+9·113	+31·53

v, $\lambda = 4358{\cdot}3$:

0·0°	−12·29	1·1614	−42·85	−148·3
17·0	−9·392	1·1451	−33·22	−114·9

These were taken by rough adjustment; at other temperatures the violet was unreadable.

iso*Butyl Diacetyl*-d-*tartrate in* o-*Nitrotoluene* (continued).

$p=58{\cdot}86$.

Densities determined:

t	16·05°	39·6°	69·6°	99·3°
d	1·1188	1·0968	1·0687	1·0405

The rotations were taken in a 50 mm. tube.

r_1, $\lambda=6716{\cdot}3$:

t.	α (100 mm.)	*d.*	[α]	[M]
0·0°	+2·256	1·1338	+3·381	+11·70
46·7	3·326	1·0902	5·184	17·94
99·1	4·580	1·0408	7·477	25·87
147·0	5·630	0·9954	9·612	33·26

r_2, $\lambda=6234{\cdot}3$:

0·0°	+1·978	1·1338	+2·964	+10·26
46·7	3·410	1·0902	5·315	19·08
99·1	4·990	1·0408	8·146	28·19
147·0	6·404	0·9954	10·933	37·83

y, $\lambda=5790{\cdot}5$:

0·0°	+1·408	1·1338	+2·11	+7·30
46·7	3·350	1·0902	5·221	18·07
99·1	5·390	1·0408	8·798	30·44
147·0	7·190	0·9954	12·274	42·47

g, $\lambda=5460{\cdot}7$:

0·0°	+0·608	1·1338	+0·911	+3·15
46·7	3·084	1·0902	4·807	16·63
99·1	5·618	1·0408	9·170	31·73
147·0	7·728	0·9954	13·193	45·65

b, $\lambda=4959{\cdot}7$:

0·0°	−2·348	1·1338	−3·518	−12·17
46·7	+1·618	1·0902	+2·522	+8·73
99·1	5·494	1·0408	8·969	31·03
147·0	8·294	0·9954	14·16	49·00

v, $\lambda=4358{\cdot}3$:

0·0°	−12·21	1·1338	−18·30	−63·31
46·7	− 3·982	1·0902	−6·21	−21·5
99·1	+5·72*	1·0404	+9·34	+32·3
147·0	Could not be read.			

* With rough adjustment; very difficult to read.

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[*Received, August 4th,* 1916.]

LXXXV.—*The Influence of Solvents, Etc., on the Rotation of Optically Active Compounds. Part XXII. Rotation-Dispersion.*

By Thomas Stewart Patterson.

In the foregoing paper the rotation data for several active compounds, and their variation with wide change of external circumstances have been discussed, and some notion of the problem to be faced on attempting to correlate rotatory power with chemical constitution—a task which has not yet even been begun—can be gathered from the results. The data collected are the most complete thus far obtained, in the sense that they include all the variables which it is possible at present to investigate, namely, constitution, solvent action, temperature, and colour of light; they therefore provide hitherto unexampled material for a fuller examination of the subject as a whole than has previously been possible, and in this paper the problem of rotation-dispersion will be dealt with from a comprehensive point of view, and regard taken to such modern work by other authors as bears on the question.

It is only within recent years that much systematic investigation has been carried out in this direction, and as generally happens in the early development of a subject, there is a certain amount of obscurity as to the meanings to be given to some of the terms used in describing the observed phenomena, and this applies in the present case even to the definition of what is known as the dispersion ratio itself.

In the early days of optical activity it was supposed that the specific rotation of a compound would be a genuine constant independent of external conditions, and although this expectation was grievously disappointed, there still exists a hope that dispersive power may prove to be sufficiently independent of external conditions to serve for the definite characterisation of the substance to which it pertains.

The dispersion ratio generally used is simply the quotient of the rotation for one colour of light by the rotation for some other colour, but, as will be shown later, numbers for rotation-dispersion calculated in this manner may vary for quite slight changes of external conditions, such as temperature, between +infinity and −infinity, a circumstance which obviously robs this ratio of any value whatever (see Winther, *Zeitsch. physikal. Chem.*, 1902, **41**, 205).

This point may be exemplified by some work of Pope and Winmill (T., 1912, **101**, 2309), who have collected rotation data for

three colours of light for some derivatives of *l*-tetrahydroquinaldine. They found (see table I, columns 3 and 4) that the rotation in four different solvents, of the benzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl, and *p*-toluoyl * derivatives have all high values, roughly speaking, of about the same order of magnitude, and that for these substances the dispersion-coefficients (column 6) are also of much the same value. On the other hand, however, the rotations of the *o*-nitrobenzoyl derivative are much smaller, and, in addition, sometimes positive and sometimes negative, giving, therefore, dispersion-coefficients not at all in harmony with those for the other compounds with which one might reasonably expect them to be strictly comparable. Whereas the first-mentioned substances have for the dispersion ratio Hg_g/Hg_y values in the neighbourhood of 1·6, those for the *o*-nitrobenzoyl derivative vary from 1·484 through 0·526 to −0·153 and −2·75. Pope and Winmill therefore regard this substance as exhibiting quite abnormal rotation constants, whilst Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 391) think that a special explanation is required to account for its peculiar behaviour. It is, however, always to be regretted if special explanations have to be invented in order to meet individual cases, particularly in instances like the present, where the singularity in the results is mainly due to the dispersion curves for the solutions of the *o*-nitrobenzoyl derivative crossing the axis of zero rotation, thus forming an example of what P. F. Frankland has aptly termed spurious anomalous rotation-dispersion (*Trans. Faraday Soc.*, 1914, **10**, 91).

These examples, together with many others which might be quoted, appear sufficient to show that there is something fundamentally wrong in the manner of calculating this dispersion-coefficient, or, alternatively, that if this method of calculation is correct, the dispersion-coefficient is a function of no value whatever as a characteristic constant for any given active substance.

The dispersive power, in order really to be useful, must remain constant, or at least approximately so, with varying circumstances, and not have arbitrary normality or anomalousness in accordance with purely accidental circumstances, such as a very slight change of temperature, or solvent, or concentration.

The first step towards reconciling results such as those quoted is to attempt so to calculate the ratios that they shall show at least an approximate constancy. In the preceding paper it has been shown to be possible to establish a connexion between the rotation of related active compounds by studying the displacement of some singular point common to the temperature-rotation curves. This

* The author prefers the name *p*-toluyl for this radicle.

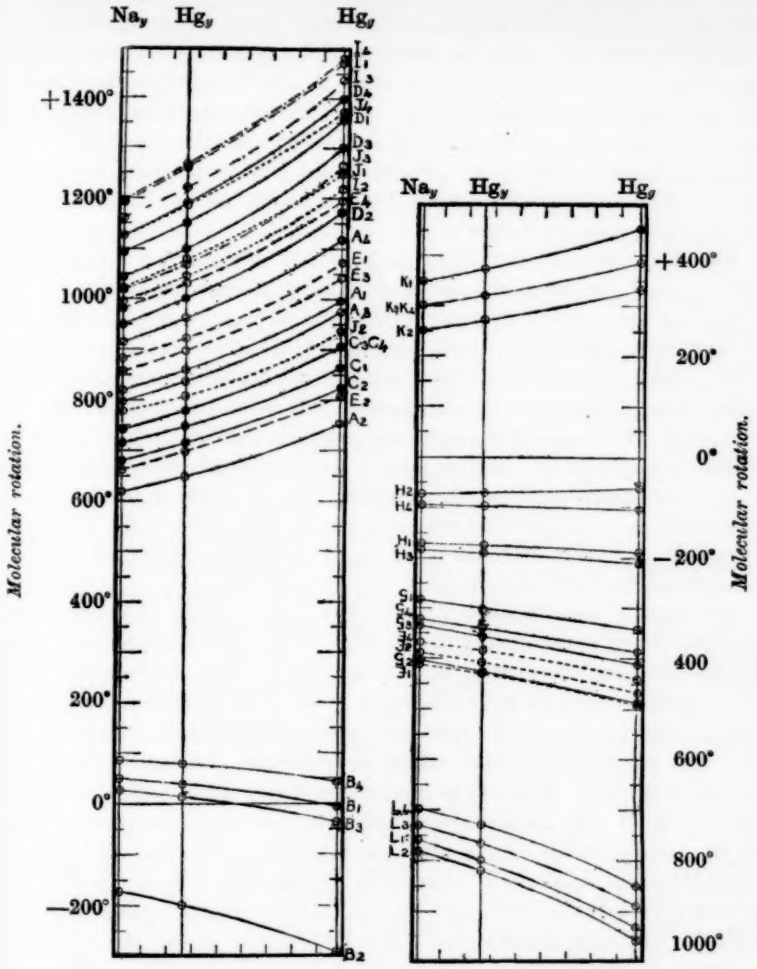
may either be the maximum which often occurs within the range of ordinary temperatures, or can be brought into view by raising or lowering the temperature, or by the action of different solvents; or it may be the point at which the temperature–rotation curves for two different colours of light intersect. We must, in the first place, find some characteristic point such as these, and this is quite possible.

It has been shown by Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 177) that the rotation-dispersion for a series of related substances, such as the esters of tartaric acid, usually plot out as a family of curves in which the change of shape is quite gradual in passing from one member of the series to another, whence it might be expected that the rotation-dispersion curves for derivatives of tetrahydroquinaldine would show a similar behaviour. When Pope and Winmill's data are plotted on a diagram, however, they certainly do not blend in a manner giving the impression of such a family of curves; on the contrary, the curves intersect at various angles. If, however, the benzoyl derivatives be plotted on one diagram and the sulphonyl derivatives on another, as is done in Fig. 1, there is clearly something common in regard to the rotation-dispersion of each set of these compounds, something certainly not reflected in the ordinary dispersion-coefficients. The diagrams present a similar appearance, the curvature in the lower part of each set of graphs being the opposite to that at the top, and changing quite gradually in passing through the figure. In the case of the benzoyl derivatives there are no curves for rotations between 100° and 600°; the curves are more evenly distributed in the case of the sulphonyl derivatives.

Now it will be observed that in the latter case the graphs for 2-nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine are only very slightly curved, and since the position of the different dispersion curves depends on, first, the constitution of the substance; secondly, the solvent in which it may be dissolved; and thirdly, the concentration in that solvent, it is apparent that a compound of this class might exist such that, either in the homogeneous condition or in some solvent, it would give a dispersion curve lying between those for 2-nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine in benzene and acetic acid, such as would be almost a straight line.

This might be expected to occur at a molecular rotation in the neighbourhood of $-82°$, and in just the same way, but, of course, with less accuracy one might expect to find some derivative of benzoyl-*l*-tetrahydroquinaldine such that in some solvent its rotation-dispersion curve would also be almost a straight line, and from the appearance of the diagram this would probably occur in the

FIG. 1.



A = *Benzoyl-l-tetrahydroquinaldine.*
B = o-*Nitrobenzoyl-l-tetrahydroquinaldine.*
C = m-*Nitrobenzoyl-l-tetrahydroquinaldine.*
D = p-*Nitrobenzoyl-l-tetrahydroquinaldine.*
E = p-*Toluoyl-l-tetrahydroquinaldine.*
I = α-*Naphthoyl-l-tetrahydroquinaldine.*
J = β-*Naphthoyl-l-tetrahydroquinaldine.*

F = *Toluene-p-sulphonyl-l-tetrahydroquinaldine.*
G = *Nitrobenzene-m-sulphonyl-l-tetrahydroquinaldine.*
H = 2-*Nitrotoluene-4-sulphonyl-l-tetrahydroquinaldine.*
K = *Naphthalene-α-sulphonyl-l-tetrahydroquinaldine.*
L = *Naphthalene-β-sulphonyl-l-tetrahydroquinaldine.*

1 = *Alcohol.* 2 = *Benzene.* 3 = *Acetone.* 4 = *Acetic acid.*

neighbourhood of $+200°$. In these two cases, therefore, the dispersion curves might be said to originate from a straight line in the neighbourhood of $-82°$ for one set of compounds and $+200°$ for the other. It will be apparent that if the two diagrams were so placed that the rotation values $-82°$ in the one case would fall upon the rotation value $200°$ in the other and the diagrams were then superposed, the curves would blend into a diagram such that the family resemblance between the curves of the two classes would be, at least, much stronger.

The diagrams are arranged in Fig. 1,* so that this rough comparison may be effected, and it will be apparent that even if the diagrams were superimposed in the manner suggested, the graphs of the one would still not completely blend with those of the other, from which it may be concluded that the dispersion is characteristic for each set of substances, but is not the same for the two sets. There is thus something which remains approximately constant throughout each diagram, and it seems possible, from a qualitative point of view, at any rate, that a rotation in the neighbourhood of $-82°$ in the one case and $200°$ in the other might be regarded as a sort of zero point from which these curves may be considered to take their origin.

Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 392), starting from their theory as to the cause of anomalous rotation-dispersion (see succeeding paper, p. 1207), have introduced what they term "characteristic diagrams." In these diagrams, rotations for different colours of light are plotted relative to the rotation for one particular colour taken as reference, instead of relative to wave-length. They thus make the tacit assumption that the spreading of the rotation values—the dispersion—is proportional to the actual value of the rotation for a given colour, and a little consideration will show that this is merely a new method of plotting rotation-dispersion curves, which could quite well be arrived at independently of any hypothesis as to the cause of anomalous rotation-dispersion.

It is then found in general that the rotation values for different colours of light lie, approximately, along a straight line. The inferences which can be drawn from these characteristic diagrams are practically those which may be made from the ordinary rotation-dispersion curves, but the characteristic diagram has the advantage that it gives a rather greater definiteness to the estimation of the position of the new zero, from which, as has been suggested above, dispersion curves, such as those for the derivatives of tetrahydro-

* In order to make the block of suitable size, the arrangement of the diagrams has been altered.

quinaldine may be supposed to take their origin, since this particular singular point for any two given colours is just the point of intersection of the two corresponding lines in Armstrong and Walker's diagram.

This will be seen from Fig. 2, where the data of Pope and Winmill are represented in the form of a characteristic diagram. The figure is drawn, however, not according to Armstrong and Walker's method, but by one which, in the author's opinion, is an improvement, admitting as it does, first, of a reduction in size of the diagram, and secondly, of an exaggeration of the vertical with reference to the horizontal scale, in cases where any such exaggeration should be desired, and it usually is desirable. A horizontal line is taken as reference line, and along it are plotted the rotations for some particular colour, in this instance mercury-yellow. At any given rotation for mercury-yellow there are plotted above and below, not the actual rotation values for the other colours involved, but the differences between these rotation values and the corresponding values for mercury yellow. Thus in the present case:

$$d_1 = \mathrm{Hg}_\gamma - \mathrm{Hg}_y. \quad d_2 = \mathrm{Na}_y - \mathrm{Hg}_y.$$

Positive values are then plotted upwards from the reference line and negative values downwards.

Thus for *p*-nitrobenzoyl-*l*-tetrahydroquinaldine in benzene we have:

$$d_1 = 1174° - 1000° = 174°. \quad d_2 = 949° - 1000° = -51°.$$

For the point B_2, representing the data for *o*-nitrobenzoyl-*l*-tetrahydroquinaldine in benzene, we have:

$$d_1 = [-289{\cdot}3°] - [-194{\cdot}9°] = -94{\cdot}4°.$$
$$d_2 = [-170{\cdot}8°] - [-194{\cdot}9°] = +24{\cdot}1°.$$

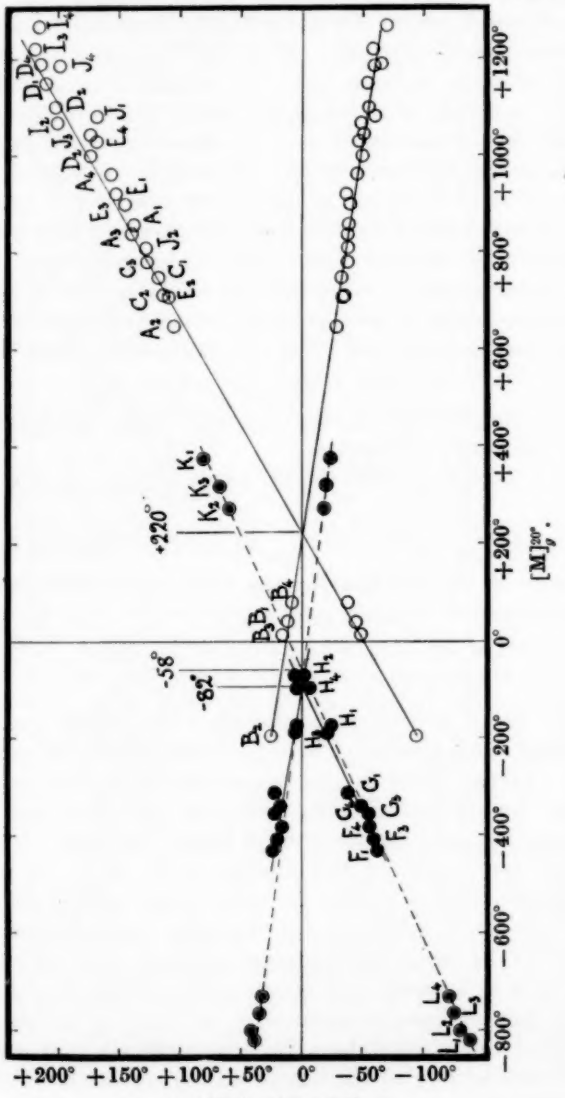
A little care is necessary in plotting these points and in interpreting them when plotted. The actual rotation at any point on the line for a given colour is the horizontal distance from the zero point plus the vertical distance from the reference line.

The figure suggests the presence of three characteristic diagrams. The points for violet for the substances *A*, *B*, *C*, *D*, and *E* lie approximately, but, it should be noted, only approximately, on a straight line which intersects the reference line at about +220°; *F*, *G*, and *H* lie upon two different straight lines which cut the reference line at a rotation of about −82°; whilst *K* and *L* appear to have a pair of lines to themselves intersecting at about −58°. At the same time it must be noticed particularly that some of the points lie considerably off the line to which, presumably, they belong, and, in addition, that the three lines of each diagram do not necessarily meet at a single point; the point of intersection is not the

same for the reference line and mercury-green, as it is for the reference line and mercury-yellow, which, of course, constitutes what is generally known as anomalous rotation-dispersion.

FIG. 2*.

Characteristic diagram for various derivatives of l-*tetrahydroquinaldine.*



* For key to lettering see Fig. 1.

It is an odd fact that Armstrong and Walker, the inventors of these characteristic diagrams, as well as Pickard and Kenyon, and others who have worked with such diagrams, should have failed altogether to point out what is by far their most important significance, and should have neglected to follow its guidance. If two corresponding series of points lie along two straight lines, then, obviously, the distances between these points are proportional to their distance from the intersection of the two lines, and we are thus quite naturally led—from a study of the facts, and not from preconceived ideas—to a suggestion for a new and more satisfactory method of calculating dispersion ratios. The point indicated by the intersection of two lines on the characteristic diagram should be regarded as a rational zero for these colours, and the dispersion-ratios must, if calculated with reference to this point, show something like a real constancy.

It is of interest to apply this idea in various directions, and in table I are given figures for the compounds examined by Pope and Winmill. In columns 3 and 4 are entered the actual molecular rotations quoted by these authors, for, as a rule, their most concentrated solutions; column 5 gives the rational zero for the substances and colours in question, whilst column 6 contains the dispersion-ratios calculated in the ordinary manner for mercury-green/mercury-yellow. In column 7 is given the ratio obtained by subtracting $+220°$, $-82°$, or $-58°$ respectively from each of the molecular rotations in columns 3 and 4, and dividing, the quotient representing the dispersion ratio calculated with respect to the rational zero. Thus the dispersion ratio for benzoyl-*l*-tetrahydroquinaldine in benzene has the value $\frac{753° - 220°}{648{\cdot}4° - 220°} = 1{\cdot}2454$.

On comparing columns 6 and 7 it will be seen that in the case of benzoyl-*l*-tetrahydroquinaldine Pope and Winmill's ratios, being those of larger numbers, necessarily show a slightly greater constancy. It is on comparing ratios for substances which by the older method give "abnormal" values or for those which differ greatly in rotation, especially when some have positive and some have negative values, that the advantage of this new method becomes evident. In the case of *o*-nitrobenzoyl-*l*-tetrahydroquinaldine the rotation values lie on both sides of the zero of rotation, as is apparent from Fig. 1, and, as a necessary consequence of this, the dispersion ratios by the ordinary method are sometimes negative and sometimes positive, and vary within wide limits.

It will be seen that the method of calculation now advocated does away entirely with the anomaly, and brings the dispersion ratios for this substance completely into line with those for the simple

Table I.

Dispersion-coefficients Calculated by Different Methods.

Substance.	Solvent.	$[M]_D$. Hg_g.	$[M]_D$. Hg_y.	Rational zero.	Dispersion ratio Hg_g/Hg_y. Pope and Winmill.	Dispersion ratio Hg_g/Hg_y. Patterson.
Benzoyl-*l*-tetrahydroquinaldine	Alcohol	+997·0°*	+859·0°*	+220·0°	1·1606	1·2159†
	Benzene	753·0	648·4	+220·0	1·1613	1·2442
	Acetone	976·4	836·6	+220·0	1·1670	1·2267
	Acetic acid	1117·5	960·8	+220·0	1·1631	1·2114
m-Nitrobenzoyl-*l*-tetrahydroquinaldine	Alcohol	865·6	748·0	+220·0	1·1572	1·2226
p-Nitrobenzoyl-*l*-tetrahydroquinaldine	Benzene	1173·7	1000·3	+220·0	1·1734	1·2223
	Acetic acid	1403·0	1189·2	+220·0	1·1799	1·2206
p-Toluoyl-*l*-tetrahydroquinaldine	Acetone	1043·2	898·1	+220·0	1·1616	1·2140
o-Nitrobenzoyl-*l*-tetrahydroquinaldine	Alcohol	−5·97	+39·0	+220·0	−0·1531	1·2484
	Benzene	−289·3	−194·9	+220·0	+1·4844	1·2274
	Acetone	−36·3	+13·2	+220·0	−2·75	1·2394
	Acetic acid	+42·3	+80·4	+220·0	+0·5262	1·2728
Toluene-*p*-sulphonyl-*l*-tetrahydroquinaldine	Alcohol	−493·3	−430·7	−82·0	1·1453	1·1795
	Benzene	−489·7	−427·1	−82·0	1·1466	1·1814
	Acetone	−466·9	−406·9	−82·0	1·1475	1·1847
	Acetic acid	−439·1	−382·6	−82·0	1·1477	1·1879
Nitrobenzene-*m*-sulphonyl-*l*-tetrahydroquinaldine	Alcohol	−342·9	−304·5	−82·0	1·1260	1·1725
	Benzene	−492·3	−431·6	−82·0	1·1406	1·1735
	Acetone	−411·3	−355·8	−82·0	1·1560	1·2027
	Acetic acid	−387·9	−338·3	−82·0	1·1466	1·1935
2-Nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine	Alcohol	−186·9	−172·2	−82·0	1·0853	1·1630
	Benzene	−65·5	−70·7	−82·0	0·9265	1·4600
	Acetone	−210·3	−188·3	−82·0	1·1168	1·2069
	Acetic acid	−103·9	−97·2	−82·0	1·0689	1·4408
Naphthalene-α-sulphonyl-*l*-tetrahydroquinaldine	Alcohol	+457·7	+374·1	−58·0	1·2234	1·1934
	Benzene	+331·6	+272·2	−58·0	1·2182	1·1798
Naphthalene-β-sulphonyl-*l*-tetrahydroquinaldine	Benzene	−957·9	−819·3	−58·0	1·1692	1·1820

* The numbers quoted are mostly those given by Pope and Winmill for the most concentrated solutions they examined.

† The numbers in this column are obtained by subtracting +220·0, −82·0° or −58·0°, as the case may be, from both rotation values—then dividing.

benzoyl derivative. Whereas the values as calculated by Pope and Winmill vary between $-2{\cdot}75$ and $+1{\cdot}4844$, those obtained by the new method show a very considerable constancy, since, even including the somewhat high value in acetic acid, the mean for these four solutions is 1·247 as compared with 1·222 for the benzoyl derivative.

The new method of calculation thus meets completely what was apparently regarded by Armstrong and Walker as a particularly difficult case, and reconciles the behaviour of this derivative of tetrahydroquinaldine with that of other substances to which, on chemical grounds, it ought obviously to be closely related. A few data are given also for *m*-nitrobenzoyl, *p*-nitrobenzoyl-, and *p*-toluoyl-*l*-tetrahydroquinaldine. It will be evident that on calculating a particular dispersion ratio with respect to a rational zero common to all these substances, a very considerable constancy for the class is obtained, vastly superior to anything which can be arrived at by the use of dispersion ratios calculated by the ordinary method. For these various compounds the rational dispersion-coefficient appears to have a value on the average of about 1·22 to 1·23.

Some data have also been calculated for the sulphonyl derivatives of *l*-tetrahydroquinaldine, the rational zero in this case being taken at $-82°$. Here, however, there is no very striking difference as regards the numbers obtained by the two methods, and since Pope and Winmill's ratios are those of larger numbers, the constancy is necessarily greater. Had their data included related substances having positive values of rotation, the advantages of the new method of calculation would be more evident. According to Armstrong and Walker, 2-nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine forms another exceptional case. It cannot be said that the new method of calculation introduces here any greater constancy into the dispersion values than the old, but it must be noticed that in this instance the new method is being subjected to a very severe test, since the values for the rotation in benzene and in acetic acid lie close to the rational zero, on which account the effect of experimental error becomes much accentuated. The new method is here, in fact, acquitting itself satisfactorily in exactly the same kind of circumstances as those in which the usual method so conspicuously breaks down in the case of *o*-nitrobenzoyl-*l*-tetrahydroquinaldine. In solvents producing a greater positive rotation, 2-nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine would certainly show less and less satisfactory dispersion-coefficients by the ordinary method of calculation. Already in benzene the coefficient has fallen below 1; the new method, on the other hand, would give numbers approximately constant.

In the case of the naphthalenesulphonyl derivatives, since they differ so widely in rotation, the new method of calculation shows to decided advantage. According to the older method of calculation, the dispersion-coefficients for the two substances show a considerable divergence, and, indeed, there is no general resemblance between any of these compounds at all. Taking the rational zero at $-58°$, however, the data for the two substances are at once brought into harmony, the value for the β-derivative in benzene lying intermediate between the values for the α-derivative in benzene and in alcohol. The dispersion ratios are obviously much the same as those for the other sulphonyl derivatives, but are smaller than those for the benzoyl derivatives. The benzenesulphonyl and the naphthalenesulphonyl derivatives thus appear to differ chiefly in the fact that their rational zeros are different.

It has already been remarked that just as the dispersion curves for different active substances plotted on one diagram, or the curves for one substance in different solvents, form a family, so the curves for one active substance at several different temperatures also form a family in which the shape gradually alters in a similar way. It is therefore the case that the data for a given compound at different temperatures fit approximately on a characteristic diagram in the same manner as do the data for an active compound in different solvents, and it is also to be noticed that the point at which the lines for two different colours intersect on the characteristic diagram for a homogeneous substance at different temperatures is the same as that at which the two temperature–rotation curves for these colours of light intersect. Just as already described, therefore, the point of intersection of any two temperature–rotation curves may be regarded as a rational zero, such that the dispersion ratios calculated with respect to that point might be constant. It is therefore desirable to examine existent data in this connexion.

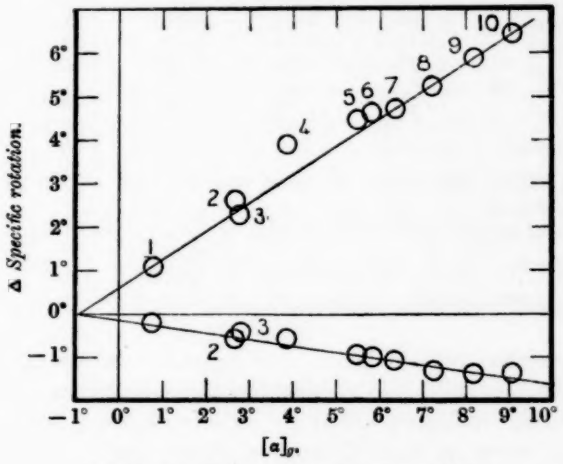
In one of the valuable papers recently published by Pickard and Kenyon (T., 1914, **105**, 1121), numbers are given for methyl-*tert.*-butylcarbinol, the rotation of which diminishes gradually as the temperature rises from 20° to 120°, at which point the alcohol boils. By extrapolation of the temperature–rotation curves, however, or by the construction of a characteristic diagram (Fig. 3), it will be seen that if the rotation continued to alter in a similar manner up to temperatures beyond the boiling point, the rotation for the three different colours would intersect very nearly at a rotation of $-0{\cdot}9°$.

In spite of the fact that the points on the characteristic diagram, both for the homogeneous substance at different temperatures and

for the solutions—excepting those for ethyl alcohol and benzene—lie very closely on straight lines, it will be noticed that the dispersion ratios calculated by Pickard and Kenyon are not constant; indeed, it stands to reason that they cannot be, but vary for Hg_v/Hg_g from 1·711 to 1·743 over the comparatively short range of temperature from 20° to 80°, but if the dispersion ratios be calculated for this particular substance in the homogeneous state and in solution according to the method already described, namely, taking the point −0·9° as the rational zero, it will be seen from table II

FIG. 3.

*Characteristic diagram for methyl*tert.*butylcarbinol.*



Pickard and Kenyon (*loc. cit.*, p. 1121).

1. *In chloroform, c=5 (approx.).*
2. *In carbon disulphide, c=5 (approx.).*
3. *In pyridine, c=5 (approx.).*
4. *In benzene, c=5 (approx.).*
5. *Homogeneous, t=100°.*
6. *In ethyl alcohol, c=5 (approx.).*
7. *Homogeneous, t=80°.*
8. ,, *t=60°.*
9. ,, *t=40°.*
10. ,, *t=20°.*

that a much greater constancy is obtained. The dispersion ratio Hg_v/Hg_g then assumes the value 1·65, approximately, throughout, which is not far from the 1·637 or thereabouts which Lowry considers to be the normal magnetic rotatory dispersion for a considerable number of compounds* (T., 1914, **105**, 83). The dispersion ratios for the solutions also come somewhere near this value, and are decidedly better than the numbers given by Pickard and

* In this connexion it may perhaps be suggested that the reason why magnetic rotation-dispersion appears to be simple more often than is the case with permanent rotation-dispersion, may be that magnetic rotation curves must necessarily take their origin from zero rotation.

Kenyon. The values for the rotations of the solutions were only determined "at the temperature of the laboratory," so that experimental errors may have crept in in this way, but it is quite obvious

TABLE II.

*Methyl*tert.-*butylcarbinol*.

Physical condition.	*t*.	$[\alpha]_D$. Hg_g.	$[\alpha]_D$. Hg_r.	Hg_r/Hg_g. P. & K.*	Hg_r/Hg_g. Patterson.†
Homogeneous	20·0°	+9·09°	+15·55°	1·711	1·647
Homogeneous	40·0	8·18	14·08	1·722	1·650
Homogeneous	60·0	7·25	12·52	1·727	1·647
Homogeneous	80·0	6·35	11·07	1·743	1·651
Homogeneous	100·0	5·50‡	10·00‡	(1·818)	(1·703)
In chloroform ...	*ca* 15·0	+0·79	+1·87	2·38	1·639
In pyridine	*ca* 15·0	2·74	5·02	1·84	1·626
In carbon disulphide	*ca* 15·0	2·70	5·32	1·96	1·728
In benzene	*ca* 15·0	3·89	7·78	2·00	1·812
In ethyl alcohol ...	*ca* 15·0	5·86	10·54	1·80	1·692

* The numbers are obtained by direct division of the numbers in columns 3 and 4.

† The numbers are obtained by division of the numbers in columns 3 and 4 after subtracting −0·9° from each, thus: $\frac{15·55+0·9}{9·09+0·9}=1·647$.

‡ These data lie off the lines in the diagram.

that the method of calculation now suggested brings the solutions better into line with the results for the homogeneous compound than does the ordinary method. This is perhaps most apparent for the solution in chloroform, for which the point lies almost exactly on the straight lines of the characteristic diagram, and yet Pickard and Kenyon's v/g dispersion ratio, 2·38, is much higher than any of the others quoted. If, however, the value be calculated by the new method, the number 1·639 is obtained, which agrees very closely, on the whole, with 1·649, the average of the values for the compound in the homogeneous condition.

Thus when the results are calculated from the rotation corresponding with the point of intersection of the lines in the characteristic diagram for any two given colours, the values show something like a real constancy, and encourage the hope that the dispersion ratio may have a general significance, and prove to be independent of external conditions.

One further and interesting example of this new method may be given, the data being those obtained by Pickard and Kenyon for *d*-1-naphthyl-*n*-hexylcarbinol. Since the small inset diagram given by these authors in Fig. 1 (T., 1914, **105**, 2646) is obviously incorrect and the large diagram on too small a scale, it was neces-

sary for the present author to re-calculate the data for the substance and then plot them on a diagram, and as the numbers used here are obtained from these latter curves, it will be found that occasionally they are not identical with those arrived at from their data by Pickard and Kenyon themselves, but the discrepancies are only small.

The curves of molecular rotation for Na_y and Hg_g intersect at a temperature of 28·6° where the rotation is +12·4°, those for Na_y and Hg_v intersect at a temperature of 34·9° where the rotation is 22·7°, whilst the curves for Hg_g and Hg_v intersect at a temperature of 36° and a rotation of +25·8°. Numbers have been calculated for all three of these ratios, but in table III below only those for Hg_v/Hg_g need be given, as they are quite sufficient to elucidate the matter in hand. Columns 2 and 3 show the actual molecular rotations for the two colours of light, and in column 4 are given the dispersion ratios as calculated by the usual method. At a temperature of 15° this ratio has a positive value, which very rapidly increases, as the temperature rises, to +15·06 at 22° and reaches +infinity at 22·7°. Immediately beyond this point the ratio would spring from −infinity and very rapidly fall, reaching the value −2·7 at 25°, and the value 0 at 28·4°. Thereafter it becomes positive again, rising slowly and arriving at approximate constancy somewhere in the neighbourhood of 100°. Clearly such a ratio can have no general value whatever.

TABLE III.

Dispersion Ratios of d-1-*Naphthyl*-n-*hexylcarbinol.*

	Intersection at [M]=25·8° t=36°			
t.	$[M]_r$.	$[M]_g$.	Ordinary dispersion-coefficient.	Rational dispersion-coefficient.
+15·0°	−55·5°	−19·6°	2·8318	1·7907
20·0	−34·0	−6·4	5·313	1·857
21·0	−30·0	−4·1	7·318	1·8662
22·0	−25·6	−1·7	15·06	1·8690
22·7	−22·9	0·0	∞	1·8877
25·0	−13·5	+5·0	−2·70	1·8894
26·0	−9·6	7·7	−1·2468	1·9558
27·0	−1·6	11·1	−0·1441	1·8640
28·4	0·0	12·0	0·0	1·8696
30·0	+5·7	15·0	+0·38	1·8611
32·5	14·5	19·5	0·7436	1·7936
36·0	25·8	25·8	1·0000	—
37·5	30·4	28·5	1·0666	1·7037
40·0	38·4	33·1	1·160	1·7260
60·0	98·2	63·8	1·539	1·9052
80·0	143·3	87·7	1·634	1·8984
100·0	175·7	105·0	1·6734	1·8927
150·0	214·8	126·9	1·6926	1·8693
200·0	208·0	123·0	1·6910	1·8746

In column 5 the dispersion ratios calculated with respect to a new zero of $+25{\cdot}8°$ are given. It will be seen at a glance that the constancy introduced in this way is, on the whole, very satisfactory indeed. Between $+15°$ and $+200°$ the lowest value of the ratio, and that in a region where experimental errors exert the greatest influence, is 1·7037, whilst the highest is 1·9558.* The dispersion ratio is thus approximately constant throughout an observed range of nearly 200°, and it may safely be asserted that the constancy would persist for some distance beyond the higher limit and probably to a much greater distance beyond the lower limit.

Much the same kind of thing obtains for the other dispersion ratios, that for the ratio Hg_g/Na_y over a wide range of temperature being approximately 1·19, that for Hg_v/Na_y approximately 2·2, and that for Hg_v/Hg_g approximately 1·87.

It seems legitimate to conclude that a method of calculation which introduces such constancy as this must be justified by some underlying cause, and the fact of this constancy seems altogether to negative the idea that the phenomena of rotation as varied by change of temperature is much complicated by secondary causes, such as polymerisation, dynamic isomerism, dissociation, etc.

On applying this idea to the data of the preceding paper, it is found that the results are of a very similar character. If the ratio of the rotations for any two colours of light be calculated with reference to the value at which these rotations become equal, they remain fairly constant over a wide interval of temperature, as table IV will show. In the table are given the values of temperature and rotation at which each of the curves for the seven other colours intersect the curve for green, and also the actual rotation values for these different colours of light at various temperatures from 0° up to 160°. In the lower part of the table are given the rational dispersion-coefficients, obtained as in the previous cases by subtracting from the rotations for the two colours concerned the rotation value at the intersection of these two curves, and then dividing.

It will be seen that the dispersion-coefficient thus calculated shows on the whole a very fair constancy. In the last horizontal line of the table are given average values for these various dispersion-coefficients. From what has been said it may be concluded that a very considerable degree of constancy for the dispersion ratios may be arrived at, provided these ratios be calculated from a rational zero.

* Values were calculated every 10° from 40° upwards.

Table IV.

Rational Dispersion-coefficients for Ethyl Tartrate.

Intersection with green at									
	t.	+0·2°	4·0°	7·7°	11·0°	21·0°	—	48·0°	91·0°
	[α]	+5·0	5·58	6·1	6·57	7·92	—	11·0°	14·27

Specific Rotations.

Temperature.	$[\alpha]_{6980}$.	$[\alpha]_{6708}$.	$[\alpha]_{6450}$.	$[\alpha]_{r2}$.	$[\alpha]_{y}$.	$[\alpha]_{y}$.	$[\alpha]_{b}$.	$[\alpha]_{v}$.
0°	—	—	—	—	5·28	4·96	3·25	−3·10
20	+6·69	6·99	7·22	7·46	7·79	7·79	6·9	2·05
40	8·10	8·43	8·79	9·13	9·90	10·16	—	6·50
60	9·17	9·57	10·00	10·47	11·61	12·07	—	10·10
80	9·98	10·45	10·97	11·52	12·92	13·6	14·42	—
100	10·62	11·16	11·76	12·32	13·86	14·73	15·92	—
120	11·11	11·63	12·30	12·93	14·50	15·58	17·04	16·58
135	—	—	—	—	—	16·03	—	17·95
140	11·34	11·80	12·63	13·34	15·00	16·15	17·83	18·23
160	—	—	—	—	—	16·53	—	19·28

Rational Dispersion Ratios.

0°	—	—	—	—	—	—	—	1·866
20	0·6058	0·638	0·6627	0·7294	—	—	1·2811	1·889
40	0·6008	0·6223	0·6626	0·7132	0·884	—	—	1·8905
60	*0·5899*	*0·6149*	*0·6533*	*0·7091*	0·8892	—	—	1·8954
80	*0·5791*	*0·6072*	*0·6494*	*0·7042*	*0·8804*	—	*1·3154*	—
100	*0·5776*	*0·6098*	*0·6559*	*0·7047*	*0·8722*	—	*1·319*	—
120	*0·5775*	*0·605*	*0·654*	*0·706*	*0·8591*	—	*1·3187*	*1·9694*
135	—	—	—	—	—	—	—	*2·103*
140	0·5686	*0·6184*	*0·6498*	*0·7067*	*0·8603*	—	*1·326*	*2·1063*
160	—	—	—	—	—	—	—	*2·217*
Means of italicised values.	**0·5810**	**0·6111**	**0·6525**	**0·7061**	**0·8660**	—	**1·3198**	**2·0989**

In the cases already considered the rational zero is different for each pair of lines on the characteristic diagram, and the dispersion is what is usually described as anomalous. It is, however, quite conceivable that the temperature-rotation curves or the lines on a characteristic diagram might meet at one single point, and if they did, this point might coincide with the zero of rotation or it might not. According to Lowry (*Trans. Faraday Soc.*, 1914, **10**, 95), the latter phenomenon "would be nothing less than a miracle," whereas "it was quite easy for a substance to have a zero rotation for all wave-lengths, and the temperature–rotation curves for all wave-lengths might easily intersect on this axis." It is unfortunate

that the evidence on which these statements are based has not been adduced, and since, in fact, there appears to be very little either way, it would perhaps be best that judgment upon the subject should be suspended in the meantime. In some of Pickard and Kenyon's later papers the lines of the characteristic diagram appear to intersect, at least very closely, in the region of zero. This is to be observed, for example, in Fig. 1 (T., 1914, **105**, 2678), the characteristic diagram for *ac*-tetrahydro-2-naphthol and some of its derivatives; also Fig. 5 (T., 1915, **107**, 44), the characteristic diagram for *l*-borneol, *d*-*iso*borneol, and their derivatives, and also Fig. 2 (T., 1915, **107**, 119), the characteristic diagram for *d*-benzylmethylcarbinol and its esters, but in no case do actual data appear to have been obtained in which several colours of light really have zero rotation simultaneously. On the other hand, Nasini and Gennari (*Zeitsch. physikal. Chem.*, 1896, **19**, 121), starting with the same assumption as Lowry as regards the cause of this phenomenon, have asserted that what they term a complete achromatism is possible at a rotation other than zero, and in certain cases Walden (*Ber.*, 1899, **32**, 2857, 2858) appears to have found such an achromatism for malic acid in a mixture of acetone and benzene and in a mixture of phenyl methyl ketone and paracetaldehyde.

If complete achromatism were only possible at zero rotation it would seem reasonable to expect that visibly anomalous rotation-dispersion would be much more marked when the temperature–rotation curves intersect at some considerable distance from absolute zero, and this does not appear, so far as can be judged from the available evidence, to be the case. In ethyl tartrate, in which the intersection takes place not far distant from zero, the intersection is over a wide range of temperature, whereas in some of Pope and Winmill's compounds, although the intersection takes place at a rotation of about 300°, the anomalous rotation-dispersion is apparently not very pronounced.

In this connexion Lowry make the further statement, "from the physical point of view, however, the line of zero rotation was a fundamental axis which differed from every other line that could be drawn, for example, it was the asymptote to which all curves of rotatory dispersion ultimately approached as the wave-length increases." There is, however, no obvious or a priori reason why light of infinite wave-length should pass through all compounds without deviation of its plane of polarisation, and it seems at present too early, lightly to adopt conclusions depending on extrapolation to infinity towards either end of the spectrum. Since it is certainly possible for the rotation (not zero) to be the same

for two colours, it is not quite clear why this is impossible for three or more.

In some recent papers (T., 1915, **107**, 1195), Lowry has attempted to get rid of the expressions "normal" and "anomalous" as applied to rotation-dispersion, and to substitute therefor the terms "simple" and "complex." His method of dealing with the question is purely deductive.* He starts by assuming the validity of Drude's equation, $\alpha=\sum\frac{k_n}{\lambda^2-\lambda_n^2}$, which, however, is based on very hypothetical grounds, and is already gravely suspect by reason of the fact that it ignores the influence of temperature on rotation. Lowry considers this factor to be practically negligible, such effects as appear to be due to temperature change being in reality caused by dynamic isomerism, but it will be shown in the succeeding paper, as is already very probable from the data of the preceding paper and the considerations of the present one, that this idea is entirely fallacious, and that the rotation of compounds in general may be greatly influenced by temperature change, quite independently of any question of dynamic isomerism. According to Lowry, however, dispersion is simple if the relationship between the rotation and the square of the wave-length plots out as a rectangular hyperbola; otherwise it is complex.

Now if the lines on a characteristic diagram intersect at a single point, this point being the zero of rotation, and if the intercepts on these lines made by any vertical ordinate plot out relatively to wave-length as a rectangular hyperbola, the intercepts made on these lines by all other vertical ordinates must plot out also as rectangular hyperbolæ, and therefore the dispersion should be simple throughout. If, however, the lines on a characteristic diagram intersected at a single point which is not the zero of rotation, then it might be possible that the intercepts on these lines made by some one vertical ordinate would plot out relative to wave-length as a rectangular hyperbola, but if so, this relationship will not hold for any other intercept in the whole system. If, however, the values of the intercepts were calculated with reference to a rational zero and the hyperbolic relationship held for one ordinate, it would hold for all others. Similarly, if the lines of the characteristic diagram do not meet at a single point, but, as appears to be most generally the case, over a range, then it may again be possible that some one intercept on these lines would give

* It is probably more in consonance with scientific principles to pursue the inductive method and base our conclusions on the observed facts rather than on speculative hypotheses.

values plotting out relative to the square of the wave-length as a rectangular hyperbola, but, again, this would hold for no other ordinate in the system. If, therefore, the absolute zero of rotation be adhered to as a fundamental point which must be implied in all dispersion ratios, it is perfectly clear that the occurrence of simple dispersion in any particular case, excepting those in which the lines of the characteristic diagram meet on the axis of zero rotation, is but an accidental circumstance, one chance out of many millions, and can have only this very restricted significance. Lowry says: "The dispersion curves were fundamental. In plotting them nothing was altered but the wave-length of the light that was used to test the properties of the substance; the substance itself remained unchanged and in the same condition throughout. . . . The temperature–rotation curves, on the other hand, included all the secondary changes produced by rise of temperature in a liquid, such as depolymerisation, dissociation of complexes of solvent and solute, etc. Under these conditions, simplicity of form could scarcely be expected, nor could the significance of the curves be understood until the various physical and chemical factors which they involved had been disentangled" (*Trans. Faraday Soc.*, 1914, **10**, 95). This, however, does not make it in any way clear what special significance attaches to a dispersion curve which, by chance, happens to be simple. The simplicity may be due to the pure active compound or to a mixture of individuals produced by these secondary changes which he postulates, provided, of course, that they occur. On either side of a region in which simplicity had been found we should have complexity, the interpretation of which again would be practically impossible. Any classification of the dispersion ratios of active substances as complex or simple is only useful provided the simplicity or the complexity persists over a fair range of temperature or dilution or change of solvents; otherwise it has little value, as it does not appear to indicate anything in particular.

Since, as has been demonstrated above, a considerable degree of constancy is introduced into the dispersion ratios by calculating them from a rational zero, it seems not unlikely that in future it may be possible to classify active compounds as normal or anomalous according as their temperature–rotation curves intersect at a single point or over a range, and it is highly probable that the latter will turn out to be normal in the sense that most substances will conform to this behaviour.

It has been shown a few pages back that when the dispersion ratios are calculated in the case of ethyl tartrate with respect to rational zero points, then, over a considerable range of temperature

for any two given colours, a fairly constant dispersion ratio may be obtained. It is therefore of interest to ascertain whether the average values shown at the foot of table IV would plot out as a rectangular hyperbola with regard to the square of the wave-length or not. If the curve thus obtained is a rectangular hyperbola, then the reciprocals of the rotation values should plot against the squares of the wave-lengths as a straight line. If this test is applied, the following data are found:

	1.	2.	3.	4.	5.	6.	7.	8.
λ	0·6980	0·6708	0·6450	0·6232	0·5769	0·5461	0·4960	0·4358
λ^2	0·4872	0·450	0·416	0·3881	0·3328	0·2982	0·246	0·1899
[α]	0·5810	0·6110	0·6524	0·7061	0·8680	1·000	1·3198	2·0989
1/[α]	1·721	1·637	1·533	1·416	1·152	1·000	0·7577	0·4765
1/[α] calc.	1·857	1·690	1·533	1·407	1·155	0·995	0·7577	0·5000

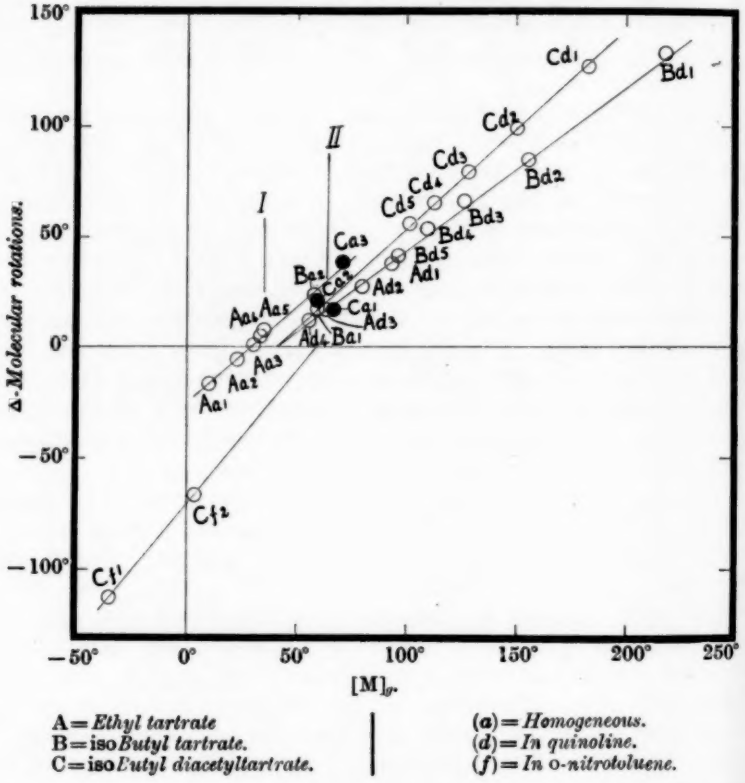
The points 3, 4, 5, 6, and 7 for 1/[α] lie almost exactly on a straight line, 2 being slightly and 1 and 8 rather further off it. Considering the manner in which the data have to be obtained and calculated, the agreement is remarkably close, and appears to indicate that even the anomalousness of ethyl tartrate may be rendered normal if only the rotation data be calculated with respect to rational zero points. The result is very different indeed from that obtained when the dispersion ratios are calculated in the ordinary way at some given temperature. It would thus appear from what has been said that there is not a little hope of bringing into a reasonable harmony over a fairly wide range of temperature or set of circumstances the dispersion data even for a compound with such marked anomalous rotation-dispersion as ethyl tartrate.

We may now turn to another aspect of this question of dispersion. In Fig. 4 is given a characteristic diagram for ethyl tartrate, *iso*butyl tartrate, and *iso*butyl diacetyltartrate at different temperatures and in different solvents for green and violet values only. It will be observed from the figure that the line Aa_1, Aa_2, Aa_3, Aa_4, Aa_5 curves upwards at that part of the diagram which represents high temperatures, namely, the right hand side. An examination of the temperature–rotation curves shows this to be due to the fact that the maximum rotation is reached for the different colours of light at different temperatures, in consequence of which the dispersion ratios are bound to vary considerably in the neighbourhood of the maximum value. If the maximum for the different colours of light is reached at or very near the same temperature, this curving would not take place, but we are led in either case to consider what happens to the characteristic diagram when dispersion ratios are measured beyond these maximum values. It will be clear from a consideration of Fig. 1, *D* (Part XXI.), that beyond the maximum the characteristic diagram

must return on itself, since the rotation for the reference colour, green, having passed its maximum, begins to diminish again. If the compound be dissolved in some substance which raises the rotation, like quinoline (see Fig. 2, Part XXI.), the data will now, generally speaking, lie along the lines of the characteristic diagram for the homogeneous compound, but they will extend to the right of the diagram beyond the point at which the data for the homo-

FIG. 4.

Characteristic diagram for various tartrates.



A = *Ethyl tartrate*
B = iso*Butyl tartrate.*
C = iso*Butyl diacetyltartrate.*

(*a*) = *Homogeneous.*
(*d*) = *In quinoline.*
(*f*) = *In* o-*nitrotoluene.*

geneous compound began to return on themselves, and when the maximum rotation in this particular solvent is reached, will return on themselves also, exactly the same kind of thing holding for a solvent of a still more powerful character, and so on. Thus in successively powerful solvents the rotation data lie approximately along the lines of the characteristic diagram up to a certain point and then begin to pass down it again. In Fig. 6 (Part XXI.)

the data obtained from the temperature–rotation curves for the homogeneous active compound would pass up, or to the right of, the characteristic diagram until the value α for green is reached, and then begin to descend it again, whereas in quinoline the values pass up the diagram until the value β for green is reached, when they also begin to pass down it. In Fig. 4 the vertical line *I* marks the position on the diagram at which this would occur for homogeneous ethyl tartrate, and the line *II* marks the point at which it would occur for ethyl tartrate dissolved in salicylaldehyde ($p=20{\cdot}214$). In quinoline the point would be well beyond the right of the diagram.

It becomes, then, of considerable interest to discover whether these data on descending the diagram lie along the original lines or not. The temperature–rotation curves above the maximum value may perhaps be tending towards some new point of intersection which, however, they certainly do not actually reach. It is unfortunately not possible to calculate values for homogeneous ethyl tartrate or *iso*butyl tartrate, since the temperature–rotation curves cannot be followed sufficiently far beyond the maximum.* Thus it might be expected that all the data which lie upon the upward part of the curve, that is, from *c* to *g* in Fig. 1, *D* (Part XXI.), should lie on one set of lines, whilst data obtained from the parts of the curves from *g* to *l* may lie on a different characteristic diagram, and those again taken from the parts of the curves from *l* to *o* may lie on a third. In the first place, it will be clear that the portions of the curves from *g* to *l* tend to cut, although they do not actually intersect at a point or points the rotation values of which would not be much different from that at which intersection takes place at *ef*, and that, therefore, if two characteristic diagrams actually exist it would be somewhat difficult to distinguish between them. The same would probably apply for the third diagram for the curves from *l* to *o*.

The question whether data taken from the parts of the curves from *c* to *g*, Fig. 1, *D* (Part XXI.), lie on one characteristic diagram and those beyond it, *g* to *l*, lie on another, may be examined by means of the data in table V. The v/g dispersion ratios calculated for homogeneous ethyl tartrate by the ordinary method are, of course, very variable, passing from a negative value to positive values through infinity between 0° and 20°. If calculated, however, from a rational zero of $+29{\cdot}4°$, a fair degree of constancy is reached, as has already been shown. The dispersion for the ester

* It is clear, of course, that in the case of a substance like ethyl tartrate, since the maxima are reached at different temperatures for the different colours, the dispersion ratios calculated by any method are bound to differ more or less on the two sides of the maximum.

in quinoline ($p=13{\cdot}601$) calculated by the ordinary method gradually diminishes from 1·4325 at −11·5° to 1·2172 at 65·15°. If calculated from the same rational zero, 29·4°, as was used for the homogeneous ester, numbers are obtained which also, although somewhat better, are not constant, varying from 1·6007 at −11·5° to 1·4655 at 65·15°. On the characteristic diagram which is shown in Fig. 4, however, the points for ethyl tartrate in quinoline and for *iso*butyl tartrate in quinoline, provided the molecular rotation be plotted,* lie approximately along a straight line which intersects

TABLE V.

Dispersion Ratios.

Ethyl Tartrate (Homogeneous).			*Ethyl Tartrate in Quinoline.* $p=13{\cdot}601$.			
$t.$	$[M]_r/[M]_y$ (ordinary).	$[M]_v/[M]_y$. (Rational zero +29·4°.)	$t.$	$[M']_r/[M]_y$ (ordinary).	$[M]_v/[M]_y$. (Rational zero +29·4°).	$[M]_v/[M]_y$. (Rational zero 40°).
0°	−0·625	1·866	−11·5°	1·4325	1·6007	1·699
20	+0·263	1·889	0·0	1·401	1·5846	1·7004
40	0·640	1·890	16·83	1·3456	1·5473	1·6936
60	0·837	1·895	44·46	1·2673	1·501	1·688
			65·15	1·2172	1·4655	1·792

iso*Butyl Tartrate in Quinoline.* $p=20{\cdot}066$.

$t.$	$[M]_r/[M]_y$. (Ordinary)	$[M]_v/[M]_y$. (Rational zero +40°).
0·0°	1·603	1·738
39·35	1·538	1·724
69·75	1·521	1·762
99·5	1·488	1·768
147·5	1·435	1·954

the green reference line at a rotation very near 40°, and if the dispersion-coefficient be calculated from this rational zero, numbers are obtained, as shown in the table, which, between −11·5° and 44·46°, vary very little indeed. These dispersion ratios are dis-

* It is stated by Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 177), that the dispersion curves for methyl, ethyl, and *n*-propyl tartrates only plot out as a family if specific rotation be used, and Pickard and Kenyon suggest something of the same sort for their characteristic diagrams. If this is the case it certainly is a very remarkable fact. In the present instances there does not seem to be a very great deal to choose between diagrams drawn from values for specific rotation or for molecular rotation, but, on the whole those for molecular rotation appear to be better. At any rate, plotted as molecular rotation, points for ethyl tartrate in quinoline and *iso*butyl tartrate in quinoline fall along nearly the same straight line, whereas this is not the case if values for specific rotation are plotted.

tinctly lower in value than those obtained for homogeneous ethyl tartrate calculated from the rational zero, 29·4°.

The corresponding dispersion ratios calculated for *iso*butyl tartrate in quinoline ($p=20{\cdot}066$) from the rational zero, 40°, show a very considerable constancy and a value at least not far removed from that for the ethyl ester. In both cases the value of the dispersion ratio at the highest temperature quoted is greater than the others, but this is doubtless due to the fact that in this neighbourhood the curves are close to the minimum value where experimental errors are likely to be magnified, and, in addition, are in a region where the curves very probably pass on to a new characteristic diagram.* It would thus appear that for ethyl tartrate the dispersion-coefficient calculated from the temperature–rotation curves from *c* up to *g* of Fig. 1, *D* (Part XXI., p. 1141), can be referred to one rational zero, and that those on the other side of the maximum, that is, from *g* to *l*, should be calculated from another, but this rational zero, as it happens, is not very far distant from the former. It seems quite possible that in other cases they may differ greatly.

Some other points connected with those dealt with above are brought out by the characteristic diagram, Fig. 4, the data for which are given in table VI. The reference line is for green; the others are all for violet as referred to green. It may be noticed that the point for homogeneous *iso*butyl tartrate, $B(a)2$, $t=226{\cdot}3°$, falls apparently on the same line as those for homogeneous ethyl tartrate, where perhaps it might not be expected, since it is on the high-temperature side of the maximum. On the other hand, the corresponding point for $t=73°$, $B(a)1$, which might have been expected to fall on the line for ethyl tartrate before the maximum, falls, in fact, decidedly off it. Again, the three points for homogeneous *iso*butyl diacetyltartrate lie in a very irregular manner on the diagram. The points for ethyl tartrate in quinoline and for *iso*butyl tartrate in quinoline appear to fall fairly closely on the same straight line, but those for *iso*butyl diacetyltartrate in quinoline, which might be expected to fall on the same straight line, since they represent a corresponding part of the general temperature–rotation curves, Fig. 1, *D* (Part XXI.), fall along or approximately along a different line which, however, appears to intersect the reference line at much the same rotation value. The two values for *iso*butyl diacetyltartrate in *o*-nitrotoluene fall on a line which does not appear to be closely related to any of the other lines in

* Of course it is not at all likely that the dispersion ratios can be calculated with respect to one rational zero up to a certain definite point and then with respect to another. There is doubtless a gradual variation from the one rational zero to the other.

TABLE VI.

(Data for Fig. 4.)

Molecular Rotations.

Ethyl tartrate		1. $t=0{\cdot}0°$	2. $t=50{\cdot}0°$	3. $t=100{\cdot}0°$	4. $t=150{\cdot}0°$	5. $t=190{\cdot}0°$
Homogeneous ...	*g.*	10·27	23·01	30·34	33·68	34·61
A(*a*)*	*v.*	−6·38	17·30	31·20	38·68	42·02
In quinoline ...		1. $t=0{\cdot}0°$	2. $t=16{\cdot}82°$	3. $t=44{\cdot}5°$	4. $t=65{\cdot}1°$	
$p=13{\cdot}601$.	*g.*	93·56	79·7	63·03	55·13	
A(*d*).	*v.*	131·10	107·2	79·88	67·11	
*iso*Butyl tartrate		1. $t=73{\cdot}0°$	2. $t=226{\cdot}3°$			
Homogeneous	*g.*	59·66	57·56			
B(*a*).	*v.*	77·78	81·11			
In quinoline.....		1. $t=0{\cdot}0°$	2. $t=39{\cdot}35°$	3. $t=69{\cdot}75°$	4. $t=99{\cdot}5°$	5. $t=147{\cdot}5°$
$p=20{\cdot}066$.	*g.*	218·4°	155·8	126·2	109·7	96·04
B(*d*).	*v.*	350·1	239·8	191·9	163·2	137·80
*iso*Butyl diacetyl tartrate		1. $t=0{\cdot}0°$	2. $t=98{\cdot}9°$	3. $t=200{\cdot}0°$		
Homogeneous	*g.*	65·56	59·86	70·35		
C(*a*).	*v.*	82·54	80·69	109·0		
In quinoline ...		1. $t=0{\cdot}0°$	2. $t=25{\cdot}0°$	3. $t=50{\cdot}0°$	4. $t=75{\cdot}0°$	5. $t=100{\cdot}0°$
$p=20{\cdot}476$.	*g.*	182·7	150·2	127·8	112·3	102·0
C(*d*).	*v.*	309·8	250·0	207·6	178·0	158·0
In *o*-nitrotoluene		1. $t=0{\cdot}0°$, $p=24{\cdot}094$		2. $t=0{\cdot}0°$, $p=58{\cdot}36$.		
C(*f*).	*g.*	−35·28		+3·15		
	v.	−148·26		−63·31		

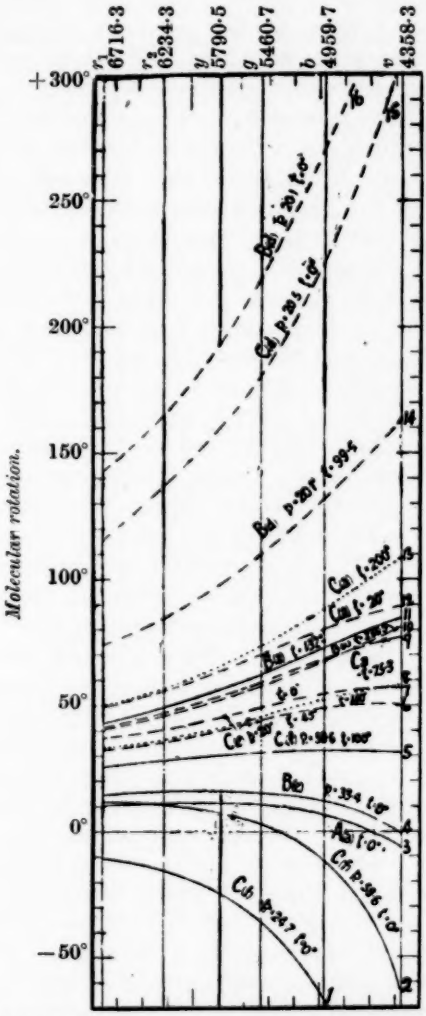
* The points on the diagram are indicated by these letters together with the number denoting the temperature. Thus A(*a*)3 represents homogeneous ethyl tartrate at 100°.

the diagram, and intersects the reference line at a rotation value of about 59°. It cannot be said, therefore, that there is any very striking definiteness about this particular characteristic diagram.

The same kind of thing can be demonstrated, and in some respects more clearly, by means of ordinary dispersion curves, such as are shown in Fig. 5. Commencing near the bottom of the diagram, the curve 3 for homogeneous ethyl tartrate is shown along with three others, numbers 1, 2, and 5, for *iso*butyl diacetyltartrate in *o*-nitrotoluene. These curves should all belong to the part *def* of the general temperature–rotation curves in Fig. 1, *D* (Part XXI., p. 1141), as is indicated by the graphs being drawn in as full lines. The agreement between these curves is clearly not satisfactory, since graphs 2 and 3 intersect quite markedly. This appears also from the direction of the lines joining the two points for *iso*butyl diacetyltartrate in *o*-nitrotoluene on the characteristic diagram of Fig. 4. The graph 11 for *iso*butyl tartrate at a temperature of

132°, the neighbourhood of the maximum, belongs to the same region of the general temperature–rotation curves. Towards the

FIG. 5.



A = *Ethyl tartrate.*
B = iso*Butyl tartrate.*
C = iso*Butyl diacetyltartrate.*

(*a*) *Homogeneous.*
(*b*) *In quinoline.*
(*c*) *In* s-*tetrachloroethane.*
(*f*) *In* o-*nitrotoluene.*

violet end of the spectrum it differs somewhat from curve 10 for the same ester at 236·5°, and, using the word in a rough and general

sense, appears to be more anomalous than the latter, which, although lower down on the diagram, is more normal in form. Curve 10 belongs to the neighbourhood *h* of the general temperature–rotation curves, Fig. 1, *D* (Part XXI., p. 1141), and therefore, together with other curves belonging to the same region, is drawn in as a broken line. A more marked difference is to be observed between the dispersion curves belonging to different regions of the fundamental temperature–rotation curves for *iso*butyl diacetyltartrate either in the homogeneous condition or dissolved in *s*-tetrachloroethane. As regards the curves for the homogeneous substance, graphs 9, 12, and 13, it is to be noticed that as the temperature rises from $-20°$ up to 75°, the dispersion curves gradually fall throughout the diagram to the position occupied by curve number 9, which represents values of the rotation at, or very near, the minimum, and then rise again with increase of temperature to the position of number 13 at 200°, and although the rotations of the ester at $-20°$ and at 200° are almost the same for red, they differ considerably for violet, the anomaly being thus decidedly greater at $-20°$ than at 200°. Curves 8 and 13 belong to the part *lmn* of the general temperature–rotation curves, and this is indicated by dotted lines. The other three curves require little comment; they all belong to the part *hikl* of the general temperature–rotation curves. Number 15, that for *iso*butyl diacetyltartrate in quinoline at a temperature of 0° ($p=20{\cdot}476$), is apparently not quite of the same shape as curve 16, representing *iso*butyl tartrate in the same solvent at almost the same concentration and temperature.

It seems probable, therefore, from what has been said, that the characteristic diagram for a particular substance will depend upon the region of the temperature–rotation curves from which the data are taken, and that any given substance may very probably have several characteristic diagrams and several rational zeros. If these rational zeros are very different in value it might be possible readily to detect the trend of the two separate diagrams. Very few data bearing on this point can be found at present in the literature, but in one of Pickard and Kenyon's recent papers (T., 1915, **107**, 117) Fig. 1 shows that the temperature–rotation curves for *d*-β-octyl 1-naphthoate are clearly approaching a maximum value, whilst those for *d*-β-octyl 2-naphthoate have passed a maximum value and are descending towards a minimum. These therefore belong to opposite regions of the general temperature–rotation curves. In another paper by the same authors (T., 1915, **107**, 35) it is shown that the data relative to the rotation of a large number of derivatives of menthol plot out apparently on two characteristic diagrams, the lines of which intersect at points considerably different.

Although little or no evidence in favour of this idea can be derived from the data given in their paper, it nevertheless does not seem impossible that the explanation may be such as has been suggested above.

From the considerations advanced in the foregoing pages the following conclusions appear to be justified. A study of dispersion curves or temperature–rotation curves leads to the idea of a rational zero. On applying this conception to rotation-dispersion it is found that a very fair constancy in the dispersion ratios may be arrived at over a wide range of temperature. In the neighbourhood of a maximum or a minimum in the temperature–rotation curves it is clear that where the maximum or minimum is reached at different temperatures for different colours no constancy can be expected. Beyond the maximum (or minimum) in the temperature–rotation curves, the dispersion curves or the points on the characteristic diagram return on themselves, whence it seems probable that the data for a given substance fit approximately on several different characteristic diagrams. Two temperature–rotation curves, for example, those for green and violet, intersect at the same or nearly the same rotation value, but, of course, at quite different temperatures, whether the compound be homogeneous or in solution. In a similar manner the corresponding temperature–rotation curves for related substances in the homogeneous state or in solution, intersect at rotation values which, although somewhat similar, are not, in general, the same. For this reason, Armstrong and Walker's characteristic diagram is only an approximation. Finally, since the dispersion curves for the same and for related active substances at widely different temperatures and in very different circumstances are only slightly different, it may be concluded that the parts played by so-called secondary causes, such as polymerisation, solvation, dissociation, dynamic isomerism, or residual affinity, are either non-existent or are very unimportant in regard to the phenomena of optical activity.

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[*Received, August 17th*, 1916.]

LXXXVI.—*The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. Part XXIII. Anomalous Rotation-Dispersion and Dynamic Isomerism.*

By Thomas Stewart Patterson.

From the results of his early work, Biot came to the conclusion that, in a solution, the active molecules simply distribute themselves unchanged amongst those of the inactive solvent, but when, later on, he found that the rotation of tartaric acid dissolved in water, in alcohol, or in wood spirit, did not remain constant with change of concentration, but gradually increased in direct linear proportion to the quantity of solvent present, he assumed a reciprocal action between the molecules of solvent and solute, converting the whole mass into a new molecular system—"une véritable tartrate d'eau liquide"—having properties different from those of the constituents, and dependent on the composition of the mixture. He thought that the active solute divides itself equally amongst the solvent molecules, so as to form homogeneous groups, always incomplete and unsaturated, the composition of the groups varying constantly with the proportions of the mixture. A similar behaviour was found for the various colours of light, except that the rate of increase of rotation with increase of dilution varied for each colour. Further study of the compounds he had originally examined, sugar, etc., showed that the behaviour of tartaric acid is not exceptional, but, in fact, the general rule, so that his theory of solution would apply in all cases.

Then tartaric acid was found to be exceptional in another respect. Whereas all other liquid media containing only one active substance, such as essence of terebenthene or camphor dissolved in acetic acid, rotate the planes of polarisation for different colours of light in direct proportion to the order of refrangibility, this acid, in solution, exhibits what is now termed anomalous rotation-dispersion.

It was noticed, further, that the solution of camphor deviates the red rays less and the yellow rays more than does essence of terebenthene, and this chance observation suggested to him that it would be of interest to pass the light through the two tubes in succession and observe the nature of the dispersion of this complex system when, from considerations based on the achromatisation of lenses, he was able to calculate the action on polarised light of two active substances of opposite rotations, but different dispersions, either in separate tubes one behind the other, or when mixed in

one tube* (*Ann. Chim. Phys.*, 1852, [iii], **36**, 431). Camphor dissolved in essence of terebenthene showed dispersion phenomena which had not been observed in media containing a single active substance, with the exception of solutions of tartaric acid (*loc. cit.*, p. 462). Biot seems to have regarded this anomaly in the dispersion of tartaric acid as favourable to his hypothesis regarding the nature of solution, but in what way he does not, apparently, explain. It is important to note, however, that although he saw clearly, and constantly referred to, the resemblance between the dispersion of tartaric acid and that of a mixture of turpentine and camphor, he was careful not to draw the conclusion that tartaric acid in solution contains two different substances, perhaps because his views as to the nature of solution did not suggest how two such compounds could arise.

This hypothesis,† quite unjustifiable on the existing data, was made later on by Arndtsen (*Ann. Chim. Phys.*, 1858, [iii], **54**, 403), who remarked that "Tartaric acid might thus be looked upon as a mixture of two bodies, differing only in regard to their optical properties, the one having a negative rotation and the other a positive rotation, the rotations varying in different proportions with the refrangibility of the light," but this suggestion cannot be regarded as any real advance on Biot, and, inasmuch as no attempt was made to propose or prove a mechanism which would provide the two modifications of the acid, it is philosophically worthless, but has nevertheless given a bias to the theory of the subject from which later workers have been quite unable to free themselves.

Nasini and Gennari (*Zeitsch. physikal. Chem.*, 1896, **19**, 113), in connexion with an investigation of malic acid in this respect, submitted the subject to a careful analysis. Adopting, they say, Biot's idea—which, as has just been explained, it was not—that anomalous rotation-dispersion is due to the presence of two or more active compounds of opposite rotations and different dispersions, they proceed to discuss how these substances may arise, remarking very pertinently that "The difficulties begin when an attempt is made to discover anything regarding the nature of these active compounds, the presence of which in solution is postulated, since, so far, it has never been possible to isolate and identify even one," a difficulty, it may be added, which has been experienced ever since.

* Biot was quite alive to the fact that in the event of the two active compounds exerting a mutual solvent effect, the result for the mixed liquids would probably not be identical with that for the same pair in separate tubes.

† Much the same thing as would be, for example, the proposal that a ship on the surface of the water is, in reality, a mixture of a balloon some distance above the surface and a submarine some distance below it.

They discuss, and reject, the supposition that dissociation in the case of a substance like malic acid or tartaric acid might furnish the two necessary different substances. They try to find what Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 79) calls a thermal lag in the case of malic acid, keeping one part of a solution at 0° for three hours and another at 80° for the same time, and then bringing both quickly to 20° and taking the rotation. "These data show that heat exercises no persisting effect, and that in all probability a definite and rapidly assumed equilibrium corresponds to each temperature" (*loc. cit.*, 126; see p. 1214). Finally, they arrive, by a process of elimination, at a last hypothesis, which, "in the opinion of Landolt, van't Hoff, and others is the most probable, and explains best the alteration in the rotation of a substance for a given ray. . . The solvent does nothing but destroy the molecular dissymmetry, the cause of the rotation. It is easy to grasp from this point of view that all the molecules are not in the same condition, and that in this way optically non-homogeneous media may arise." Some considerable difference of opinion is likely to exist, however, as to the ease with which this suggestion, depending on an entirely unknown mechanism, really can be grasped.

In a paper immediately succeeding that just referred to, Gennari (*Zeitsch. physikal. Chem.*, 1896, **19**, 130) has described the rotation phenomena in the case of nicotine and its salts. By adding nicotine to a solution of nicotine sulphate, he was able to produce a solution having anomalous rotation-dispersion, and he therefore concluded that in a solution of nicotine acetate in water the anomalous rotation is to be explained by the simultaneous presence of nicotine acetate and free nicotine. "Thus we have a new proof of the old hypothesis of the presence of two substances in solution, a lævorotatory and a dextrorotatory, which have not quite equal dispersions."

Walden (*Ber.*, 1899, **32**, 2857) and Woringer (*Zeitsch. physikal. Chem.*, 1901, **36**, 336) also did some work in this connexion, and the subject was then taken up by Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 161), whose treatment of it was very much more systematic and extensive than any other up to that time. In one of his papers (*Zeitsch. physikal. Chem.*, 1906, **55**, 257) he develops his ideas in regard to anomalous dispersion, and sums up on p. 278. He adopts chiefly as an explanation the simultaneous existence of single and double molecules, but appears also to think that the phenomenon may be caused in electrolytes, by the dissociated and undissociated molecules, and that in other cases the active molecule and a complex which it forms with the solvent may be the agents. Tschugaev (*Ber.*, 1911, **44**, 2023) seems also to regard the presence

of different molecular complexes of one active molecule, either by polymerisation or by combination with the solvent, as likely, but he introduces a further development by suggesting that the superposition of two active centres in one molecule—as, for instance, in *l*-menthyl *d*-β-camphorsulphonate—may provide the two oppositely rotating and differently dispersing radicles (see p. 1208, footnote *).

Arndtsen's original view has recently been brought into prominence again by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 388), who base their views on the behaviour of fructose, in solutions of which it may be admitted that at least two different substances are probably present, although, as happens in this case, unaccompanied by what Armstrong and Walker would call anomalous rotation-dispersion. If a solution of fructose is suddenly heated or suddenly cooled, the rotation alters and goes on altering for some time after the new temperature has been established. If an aqueous solution of fructose is diluted with alcohol the rotation alters again, and again goes on altering for some time. These facts point very definitely to a change in the equilibrium between different forms of fructose and, although both forms have not actually been isolated, the analogy to glucose is sufficiently close to justify a belief in the second form.

Armstrong and Walker therefore conclude that any compound which shows a variable rotation with change of external conditions is to be regarded as existing in at least two isodynamic forms. These have different—often opposite—rotations and, presumably, different dispersions, but the rotation and the dispersion are fixed and unalterable. When a compound is heated, for instance, the rotation changes because the equilibrium between the two forms is displaced, as is the case in solutions of fructose.

When we remember that we owe, if not exactly the modern explanation of the acetoacetic ester synthesis, at least its immediate progenitor, to Armstrong, and that the quite recent work of K. H. Meyer on various tautomeric substances may be regarded as the logical result of his suggestion, it is, perhaps, not surprising that he should favour, in connexion with the phenomena of optical activity, explanations involving dynamic isomerism. Very serious difficulties, however, present themselves in regard to the application of these views, and the present author maintains that Armstrong and Walker's analogy between the behaviour of fructose and that of, for example, ethyl tartrate, is singularly incomplete.

An attempt will be made to demonstrate this immediately, but in passing it may be mentioned that Armstrong and Walker's views have been taken up enthusiastically by a number of other chemists.

and some of the assumptions which they have found it necessary to make in order to provide the two compounds to which the anomalous rotation-dispersion is to be ascribed, must be referred to. Lowry and Dickson (*Trans. Faraday Soc.*, 1914, **10**, 58) have discussed a considerable number of ways in which two different compounds might arise from one original, and Lowry and Abram (T., 1915, **107**, 1194) have even gone so far as to suggest that anomalous rotation-dispersion can be regarded, conversely, as a proof of the existence of dynamic isomerism. According to the first-mentioned authors, "ethyl tartrate . . . may . . . contain the fixed ester, $\begin{matrix}OH\cdot CH\cdot C(OEt)_2\\ OH\cdot CH\text{——}CO\end{matrix}\!>O$, in addition to various labile forms of the ester, $\begin{matrix}OH\cdot CH\cdot CO_2Et\\ OH\cdot CH\cdot CO_2Et\end{matrix}$. But methyl tartrate, which is a well-defined, crystalline compound and resists fractionation, also shows anomalous dispersion; this cannot be attributed to ordinary static isomerism, but may be due to a dynamic isomerism of one of the more elusive types, in which the change of structure is too rapid to manifest itself by mutarotation in the freshly prepared solution" (*loc. cit.*, pp. 59, 60).

Now the phenomenon of anomalous rotation-dispersion is very similar in methyl and ethyl tartrates and, since the substances themselves are so closely analogous, it seems remarkable that it should be necessary to ascribe the phenomenon to different causes in the two cases. This, however, is only one of the many inconsistencies to which the idea gives rise.

Again, Pickard and Kenyon (T., 1914, **105**, 837) have found anomalous rotation-dispersion in quite simple esters containing only one asymmetric carbon atom, such as *d*-β-octyl acetate, and other similar substances.* According to Lowry and Dickson (*Trans. Faraday Soc.*, 1914, **10**, 60), in order to account for these cases it is necessary to postulate some "labile isomerism involving little more than a rearrangement of residual affinity," whatever that last phrase may mean,† whilst for *l*-α-naphthylmethylcarbinol some form of isomerism more elusive still has to be called in, such, for instance, as "the concrete existence of two or more of the many varieties of the

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aromatic nucleus * postulated † by organic chemists during the past fifty years," unless perhaps—Lowry suggests—the anomalous rotation-dispersion may be ascribed, in this case, to polymerisation, always a convenient refuge should other hypotheses anyway fail in plausibility.

Certainly out of this multiplicity of hypothetical causes it will always be possible to find something capable of adaptation to any given case, only a little verbal ingenuity being necessary, but, on the whole, the difficulties which Nasini and Gennari met with "whenever we attempt to learn anything further as to the nature of the two compounds" have, if anything, been increased rather than diminished. In the case of ethyl tartrate, for example, anomalous rotation-dispersion cannot be shown to be due to superposition of two partial rotations, no association with the solvent can be proved to occur, no polymerisation of the active substance can be established,‡ two different modifications of the ester have not been isolated, and the other characteristics of dynamic isomerism are altogether lacking, whilst the same may be said in regard to the simple esters and the naphthylmethylcarbinol described by Pickard and Kenyon, as well as with reference to all other active substances of the same kind.

Occasionally, but very seldom, this difficulty is recognised. Thus Pickard and Kenyon say, "It should, however, be definitely stated here that as yet no direct evidence has been obtained that any of the esters as prepared in the manner described is a mixture of two isomerides. The existence of an isomeride with a ring structure, such as Armstrong and Walker have suggested for the esters of tartaric acid, does not seem possible in the case of the esters now described, unless a form of polymerisation takes place. It seems much more probable that the existence of the two forms is due in the one case to the exercise of supplementary valencies of the oxygen atoms—a force which it is easy to conceive is weakened by an increase of temperature, and also possibly by solvents. At present it cannot be said that it is either probable, or yet improbable, that the exercise of such supplementary valencies would cause the wide variations which have been observed in the optical properties of these esters" (T., 1914,

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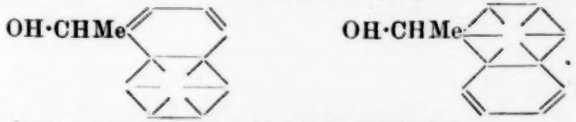

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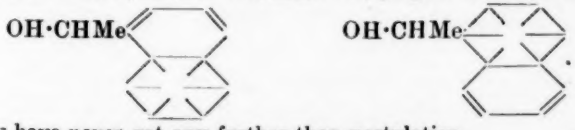

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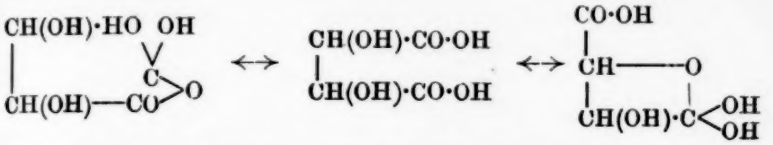
105, 843—846). Passing over the mystery as to how a particular thing can be "much more probable" than something else in one sentence, and "cannot be said to be either probable or yet improbable" in the next, it need only be remarked further that various investigators, for example, Bruhat (*Trans. Faraday Soc.*, 1914, **10**, 44), Clough (T., 1914, **105**, 56), and not a few others have adopted Armstrong and Walker's suggestion, thus basing their ideas on a few experiments of Biot's, but drawing from them conclusions from which Biot himself shrank, and wisely shrank. It would seem, however, from what has been said, that if anything can be arrived at by general consent, this point might be regarded as settled, and yet it is as far from proof as ever it was.

The primary fallacy which appears to be involved in Armstrong and Walker's reasoning, and in that of their followers, lies in supposing that because one can imitate a particular process in a certain way, the process necessarily occurs in that way. Thus an automobile and a hansom cab may both travel along a street, but it does not therefore follow that their propelling mechanisms are identical. Similarly, it is true that the phenomenon of anomalous rotation-dispersion can be imitated by a mixture of two active substances, but this, although it certainly suggests an explanation which is worth testing, cannot be accepted as a definite and general proof, unless in all cases, or at least in such a proportion of typical cases as would appear to justify its application in all cases, the two components can really be isolated or clearly demonstrated, which, of course, is very far indeed from being the case.

It may be granted that many of the rotational phenomena exhibited by solutions of fructose are due to alteration in the proportions of isodynamic forms present, but the analogy between the behaviour of aqueous solutions of fructose and the behaviour of ethyl tartrate is painfully incomplete, because the changes of rotation which take place in the fructose solutions occur only slowly, since they are dependent on slow structural changes, and on that account they are very sharply contrasted with the changes in rotation commonly regarded as due to solvent influence, which, like pressure, evidences itself instantaneously, so far as our experimental methods allow of a judgment. It is highly illogical to apply the explanation of one phenomenon directly to other cases in which the quite distinctive characteristic of the former—the characteristic by which it is known and was first detected—namely, the slow change, is absent, and this is where the most serious hiatus occurs in Armstrong and Walker's argument.

The changes of configuration which Armstrong and Walker have

suggested in the case of tartaric acid (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 399), namely:



which, by the way, are highly improbable on chemical grounds, are fairly closely comparable with the change of α-phenylnitromethane, $C_6H_5\cdot CH_2\cdot NO_2$, into β-phenylnitromethane, $C_6H_5\cdot CH{:}NO\cdot OH$, a change which can readily be measured, whilst they seem more complex, and therefore likely to be slower, than the conversion of a *syn*-oxime into an *anti*-oxime, which is also a slow change in spite of the fact that, if the ordinary formulation be adopted, it seems as simple as any case of dynamic isomerism could well be. It might therefore reasonably be expected from analogy that these changes in tartaric acid should also be slow and capable of being followed in the polarimeter. It is very questionable whether the other suggestion of Armstrong and Walker, namely:

represents a valid idea at all, or anything more than a mere form of words.

In this connexion Lowry and Dickson (P., 1913, **29**, 185), referring to ethyl tartrate, state that "slow changes of rotatory power with time, comparable with those observed in methyl camphorcarboxylate, are found to take place in the liquid ester," whilst these same authors (*Trans. Faraday Soc.*, 1914, **10**, 59) state that "as a matter of fact, ethyl tartrate appears to be a commonplace mixture, which can be fractionated by ordinary methods into portions which differ widely in their rotatory power for violet light." Taken literally, the latter statement is no doubt true, but the authors intend it to be understood that the "portions which differ widely in their rotatory power" contain active substances of dissimilar constitution, and this is more than doubtful. Even if it were the fact, however, it would militate seriously against the explanation which Lowry and Dickson advocate. The changes of rotation which occur in ethyl tartrate with change of solvent, etc., are not slow, but instantaneous, thus differing very materially from those which take place in solutions of fructose, dextrose, methyl camphorcarboxylate, etc.

In a later paper (T., 1915, **107**, 1176), Lowry and Dickson give the evidence on which they base the somewhat startling statement quoted above. Happily it proves to be much less sensational than might have been expected from the original intimation, amounting, on the evidence adduced, merely to an announcement of the fact that ethyl tartrate, like other active liquids, can be purified by fractional distillation from the inactive materials which it is liable to contain. Lowry and Dickson's remarks were, however, somewhat disquieting, because they seemed to indicate that ethyl tartrate is very difficult to prepare in a pure condition, and that the investigations carried out during a number of years past by the present author might be vitiated on this account.* With some anxiety, therefore, the data quoted on p. 1160, Part XXI., which had been obtained by the author a considerable time previous to the publication of Lowry and Dickson's paper, were turned to for examination in this connexion. These had been plotted as curves for observed rotation in a 100 mm. tube. Values were found, by interpolation, for a temperature of 20°, and then multiplied by six in order to make them comparable with those given by Lowry and Dickson. The following table shows the result:

		Lowry and Dickson.				
	λ	aA_1.	aC_3.	bA_1.	bC.	Patterson.
Li	6708	47·90	48·9	42·45	49·62	50·34
Hg ...	5780	53·15	54·6	46·17	55·80	—
Hg ...	5769	—	—	—	—	56·70
Hg ...	5461	52·70	54·27	45·39	55·80	56·40
Hg ...	4358	7·60	10·20	1·53	14·25	14·46

It may be noted that the values are, throughout, in the same sequence: bA_1 gives the lowest values for all colours, the last column the highest. The numbers under bC are the data for Lowry and Dickson's purest ester, and it will be noticed that the author's specimen, which had been made and purified in the manner customary in this laboratory for many years, is apparently somewhat purer than any of the fractions obtained by them, the rotations for all the colours quoted being slightly higher, but on the whole in fair agreement with those of these authors. The other data, aA_1, aC_3, bA_1, show the variation, particularly in the violet, to which Lowry and Dickson attribute so much importance "as showing that the variations of rotatory power do not depend on the presence of inactive or racemic ester. If this were the case, the rotations for different wave-lengths would vary proportionally from sample to sample" (T., 1915, **107**, 1177). This statement seems quite irrelevant. No *dl*-ester is likely to be produced, and even if it were it could not be removed by fractional distillation, since it boils

* See footnote, p. 1215.

at the same temperature as the pure ester. If by "inactive ester" is meant ethyl *i*-tartrate, then the statement, from a general point of view, is incorrect.

The result of fractionating ethyl tartrate is to remove small quantities of inactive substances, such as water, ethyl alcohol, and in some cases hydrogen chloride and ethyl chloride, which may be present, and the removal of these does not produce in the residue the same proportionality in the rotations for the different wave-lengths as obtained before distillation.* As is shown by most of the work of the past hundred years on the subject, the very opposite is the case. Neither additions of inactive material nor changes of temperature cause proportional variation in the rotations for different wave-lengths, and, indeed, nearly all the problems of optical activity with which we are dealing now are due to this fact. A reference to the curves of Fig. 1, Part XXI., will make this clear in regard to the influence of temperature, whilst the lower parts of Fig. 2, Part XXI., demonstrates the same point in connexion with the effect of inactive solvents. As to the former, it will be noticed that since the curve for violet for homogeneous ethyl tartrate is very much steeper in the neighbourhood of the ordinary temperature than are the others, it is necessarily more affected by slight changes of temperature—or also by slight quantities of inactive impurity—the experiments quoted by Lowry and Dickson being wholly in harmony with this statement. Any argument in favour of dynamic isomerism based on the behaviour of ethyl tartrate in this respect may, therefore, be set aside as invalid.

When the solutions of certain sugars, dextrose, *d*-fructose, *d*-galactose, *d*-xylose, lactose, and maltose, are heated to a moderately high temperature and suddenly cooled, there occurs what Hudson calls a thermal lag, which in the case of fructose has been measured, the rotation not becoming constant until several hours after the new temperature has been established (*J. Amer. Chem. Soc.*, 1909, **31**, 79). The change is here again a slow one, and not comparable with anything known in regard to the behaviour of such a substance as ethyl tartrate.

Hudson, however, was unable to detect the least indication of such a lag in the rotation of solutions of sucrose, raffinose, salicin, and arbutin, "whence," he says, "it is evident that the thermal lag (in fructose, etc.) is due to the slow establishment, in solution, of the equilibrium of the reaction which causes the mutarotation, namely, the reversible change between the α- and β-forms of the

* This would apply, of course, although perhaps not very markedly, to ethyl *i*-tartrate also. Whether it would apply to ethyl *dl*-tartrate can scarcely be said to be definitely known. Probably it would not apply.

sugars." The assumption—an eminently reasonable one—is thus made that since there is no thermal lag in sucrose, there is also no isodynamic change, and it might be expected that if this excellent argument can be applied to sucrose and salicin, which are closely related to dextrose and fructose, it ought to apply with equal force to other substances, such as ethyl tartrate and the many optically active compounds which, like sucrose, also show no lag, and all the more is this the case, since the behaviour of ethyl tartrate is entirely similar to that of sucrose, any differences being, so far as we can judge, of degree and not of kind. Thus, as has been remarked, there is no thermal lag in either case; the rotation of both compounds is influenced by change of temperature as well as by change of concentration and change of solvent; the changes at the ordinary temperature are smaller for sucrose than for ethyl tartrate, which, however, would only lead to the expectation that thermal lag ought to be detectable in ethyl tartrate much more easily than in sucrose, and that, therefore, isodynamic change is by so much less likely in the former than in the latter substance.

In the paper already quoted Lowry and Dickson (T., 1915, **107**, 1177) discuss the question of a possible thermal lag in ethyl tartrate, and show that nothing of the kind is to be observed. Instead of arriving at the above logical result, however, they draw, like Nasini and Gennari, see p. 1206, the rather odd conclusion that "the failure to detect mutarotation in ethyl tartrate cannot, however, be cited as evidence that its many anomalies * are physical, and not chemical, in their origin; it only indicates that the chemical changes produced by distillation, by dilution, and by heating and cooling pass to a position of equilibrium much more quickly than in the case of nitrocamphor."

This statement is, of course, a mere begging of the whole question. It is indeed true that a failure to detect mutarotation in ethyl tartrate does not of necessity absolutely disprove the existence of dynamic isomerism, but it undoubtedly weakens the argument in favour of dynamic isomerism very greatly indeed, and from the point of view of logic it is absurd to say that the absence of mutarotation "only indicates" a very quick establishment of equilibrium. It cannot bear this interpretation except by assuming the proposition which is to be proved, and to make this assumption compels us to a progress round the circumference of one of the narrowest of vicious circles. If thermal lag had been detected it would certainly, and with reason, have been regarded as evidence in favour of dynamic isomerism. Its absence is therefore evidence against this assumption. It is altogether wrong to claim that an

* What are these anomalies ?

experiment favours a particular hypothesis in whichever way the experiment may happen to turn out; the *capita, ego vinco; caudae, tu perdis* principle is inadmissible in science. It might, conceivably, be that the absence of thermal lag is due to a very rapid establishment of equilibrium, but to assume that it is so, to conclude first, that there is dynamic isomerism in a given case, and, secondly, that it is too rapid to be detected in that case, to eliminate, in fact, two unknowns from one equation, merely renders discussion superfluous, since, if the demonstration of thermal lag is to be a proof of dynamic isomerism and the absence of thermal lag is also a proof, or, at least, no disproof, of dynamic isomerism, there does not appear to be room for any other possibility.*

It is a very interesting fact, as showing the peculiar condition of chemical philosophy at the present time, that exactly the same argument, namely, Hudson's induction in regard to the absence of thermal lag in the case of sucrose, and Lowry and Dickson's in regard to the absence of thermal lag in the case of ethyl tartrate, should be used in these two similar instances in order to arrive at exactly opposite conclusions.

In their attempt to establish an analogy between the mutarotation of nitrocamphor and the surmised mutarotation of ethyl tartrate, Lowry and Dickson (*loc. cit.*, p. 1179) suggest that the change in ethyl tartrate might be analogous to that which occurs in the molecules of liquid water or the liquid and vapour of nitrogen peroxide when the temperature is varied, because in these no lag has been detected. It ought, however, to be remembered that in arguing from analogy comparison should be instituted, so far as possible, between similar things, and the present author submits that the mutual change of the two forms of nitrocamphor would be vastly more like any constitutional change which would take place in ethyl tartrate than the latter could resemble an establishment of equilibrium in liquid water or in nitrogen peroxide. In the two changes which one might expect to be comparable, those of nitrocamphor and ethyl tartrate, there is thermal lag in the one case and none in the other, and the only logical conclusion from this is that in ethyl tartrate there is no mutarotation.

In the paper immediately succeeding that just quoted, Lowry and Abram discuss the rotation data of methyl tartrate,† and are

* "And so this is really the primary condition of a good hypothesis—the fact whether it is capable of verification or disproof or not. Unless it is of a kind that permits of investigation, it is worthless as an hypothesis." Williams, "Logic," p. 88.

† Lowry and Abram studied this ester in preference to ethyl tartrate because it is a solid and resists fractionation. If there is anything at all in Lowry's ideas it is clear that there is little benefit in this, since the moment

there the victims of an exactly similar fallacy. There is, in fact, no evidence in favour of the existence of two forms of methyl tartrate in the liquid or dissolved condition, except—if one adopts the suggestion of Armstrong and Walker—the occurrence of anomalous rotation-dispersion, which, however, can scarcely be regarded as a proof of any theory put forward to explain itself.

In their original paper on this subject Armstrong and Walker make two most important and very arbitrary assumptions. They postulate, first, that the rotatory power of both forms of fructose is the same at all dilutions (p. 394), and secondly (p. 391), "that the rotatory power of each of the two constituent isomers is constant under all conditions," that is to say, both with change of solvent and change of temperature. They add, "the extent to which this assumption is justifiable will be discussed later on," but this promise does not appear to be fulfilled in the paper quoted. It is, however, a point of capital importance, and one which in the present author's opinion might well have been discussed to begin with, since on these premisses the whole of their argument depends.

Lowry and Dickson (T., 1915, **107**, 1185), dealing with this question, say: "The fundamental assumption that, apart from definite chemical changes, the rotatory power of a substance is constant is, however, too drastic to be more than a first approximation," and in making this admission they clearly give their whole case away. Who is to decide, and how, as to what amount of variation of rotation is due to the effect, for example, of temperature-change and what to definite chemical change, not to mention the difficulty of deciding when definite chemical change has occurred—for instance, in ethyl tartrate? If there is any change in rotation due to alteration of temperature, why may not all the change be due to this cause? Obviously, it may be, and the fact remains, that it is only legitimate meanwhile to regard, as due to mutarotation, those cases which exhibit slow change or thermal lag, and to ascribe all others, until there is some real reason to the contrary, directly to temperature effect or to solvent influence, as the case may be.

Thus a large number of hypothetical and arbitrary causes have been suggested to account, not merely for the phenomenon of anomalous rotation-dispersion, but for the effect of temperature change, as well as for the influence of solvents, on rotation. It has

the methyl tartrate becomes liquid it must necessarily suffer from all the disabilities of the ethyl ester, with which its behaviour is strictly comparable. As a matter of fact, for polarimetric investigation, it is a very great advantage that an active substance should have as low a melting-point as possible exactly for the reason that the influence of temperature-change can then be examined over a wide range.

been shown that none of these can in any way be regarded as satisfactory; none can be proved except by adducing the phenomenon which is to be explained as proof of the theory that is to explain it, a process that can scarcely be regarded as sound. It is perhaps too much to hope definitely to disprove them all, on account of the well-recognised difficulty of proving a negative, but some of them can be shown clearly to be untenable.

In this connexion it must be noticed that the various parts of Armstrong and Walker's theory are intimately bound up with one another, and therefore, that they stand or fall together. If one part of their theory can be disproved, the whole of it may be regarded as disproved also.* Their theory, so far as the present author can judge, is comprised in the statement that all rotational changes, or—in view of Lowry and Dickson's partial recantation just referred to—most rotational changes, which are due to the influence of solvents or to the effect of temperature change, as well as the phenomenon of anomalous rotation-dispersion, are always due to dynamic isomerism. It is, of course, admitted that some of these changes, namely, the temperature and solvent effects in the case of fructose, dextrose, etc., are sometimes partly due to that cause, and that the presence of two different chemical substances may give rise to the phenomenon of anomalous rotation-dispersion, but it is strenuously denied that the converse is necessarily the case, and it is asserted that in the large majority of instances such changes have no necessary connexion with the cause propounded by Armstrong and Walker.

Thus it will be clear that if, in any case, solvent influence on rotation can be definitely shown to exist where mutarotation is equally definitely shown to be absent, Armstrong and Walker's theory may, in general, be regarded as disproved.

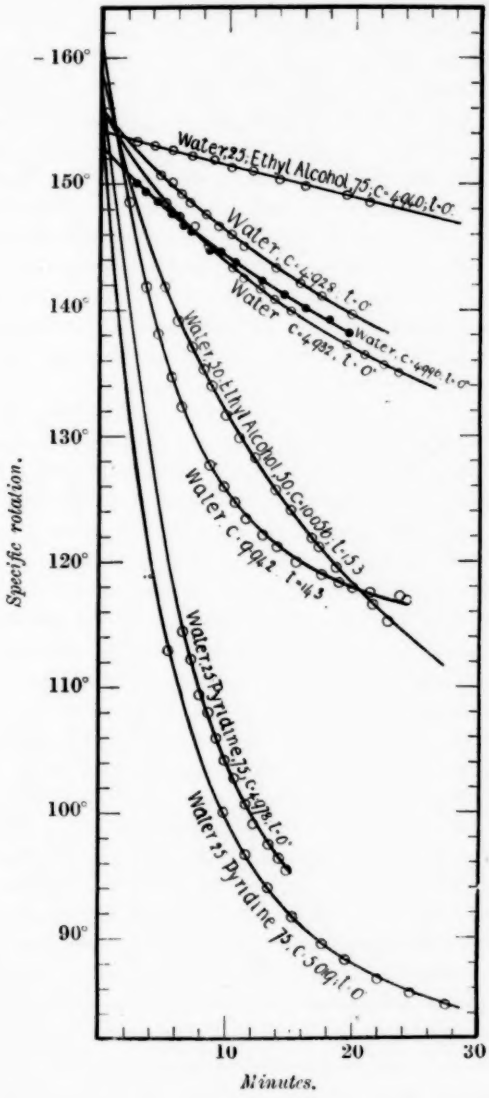
The problem which presents itself, therefore, is to find some case in which an active compound exhibits solvent, or temperature, or concentration influence, but in which dynamic isomerism is completely excluded. The investigation of this matter is quite simple, and since it would be most desirable to disprove Armstrong and Walker's theory on the ground taken up by them, we may deal in the first place with the case of fructose. When fructose is dissolved

* "Every hypothesis is bound to explain, or, at any rate, not to be inconsistent with, the whole of the facts it professes to account for; and if there is a single one of these facts which can be shown to be inconsistent with (I do not merely mean inexplicable by, but contrary to) the hypothesis, the hypothesis falls to the ground—it is worth nothing. One fact with which it is positively inconsistent is worth as much, and as powerful in negativing the hypothesis, as five hundred." Huxley, Collected Essays. II, p. 463.

in water the rotation of the solution immediately begins to change, but by making observations from time to time we can estimate the initial rotation of the solution, that is, the true rotation of a solution of pure fructose, which, of course, is independent of any considerations regarding mutarotation. If now the same fructose is dissolved rapidly in some other solvent, say, a mixture of water and alcohol, the initial rotation of the pure fructose in the new solvent can be found in the same way as before. Unfortunately, in this special case the method cannot be very satisfactorily applied, since fructose is not very readily soluble in liquids such as alcohol, benzene, chloroform, etc., and for the most part only aqueous mixtures can be used, but if the initial rotations for two different solvents are different, it must be concluded that dynamic isomerism has nothing to do with this particular phenomenon, and immediately a large part, if not indeed the whole, of Armstrong and Walker's theory goes by the board.

A number of experiments in this direction were therefore carried out by the present author. Crystallised fructose was ground into a fine powder, and weighed in a graduated flask. Water was then added to the mark, and solution of the fructose effected as quickly as possible at a constant temperature. The time of addition of the water was noted and also the time at which solution appeared to be complete. The experiment was reckoned to commence from a time intermediate between these two points. The rotations were taken by a single setting of the instrument at intervals of a minute and sometimes less in order to obtain as complete a curve as possible. The data obtained are given at the end of the paper. The constant has been calculated according to the formula used by Worley (T., 1911, **99**, 352), and considering the fact that the time was being read to seconds and that the interval between the readings was so short, the constant is as good as could reasonably be expected. The velocity of the change is decidedly greater in water than in a mixture of alcohol and water, as, of course, was already known, whilst also the change proceeded much further in the latter solution than in the former, as is indicated by the value of the rotation at infinite time. These data are plotted in the diagram. It will be recognised at once from the shape of the curves that extrapolation to zero time must necessarily be accompanied by considerable error. Although the first reading was taken for the aqueous solution at 14·3° only two minutes after the solution had been made up, it will be fairly apparent that either of these two curves might quite well be extrapolated to any value between about −158° and −162°. Unfortunately, therefore, no perfectly definite conclusion can be drawn from these experiments. It seems clear that

the solvent influence of a mixture of alcohol and water as compared with that of water itself is not very different, and might even be



identical. It was thought that a more definite conclusion might be reached if similar experiments were carried out at a lower temperature, since, on account of the reaction proceeding more slowly, a

better extrapolation to zero time could be effected. The solutions were therefore then made up as rapidly as possible at 0° and placed in a polarimeter tube surrounded by melting ice. Three solutions were prepared in water with the object of determining what degree of accuracy could be attained to in successive experiments intended to be identical. It will be seen that the difference of the extremes in these cases is between two and three degrees, whence we can only say that the value of the rotation of an aqueous solution of fructose, $p=5$, $t=0°$, at zero time lies between about $-152{\cdot}6°$ and $-155{\cdot}8°$. The main reason for the discrepancy in these results is doubtless the difficulty of making up the solutions in exactly the same way in each case. It will be noticed that in these three instances the velocity of the mutarotation is decidedly less than at 14·3°, to such an extent that one may regard the extrapolation of any single curve as decidedly more accurate at the lower temperature. Between the three, however, there is a difference of some two or three degrees.

The velocity of the mutarotation in a mixture in 25 volumes of water and 75 volumes of ethyl alcohol at 0° is, as before, considerably less than in water, the accuracy of extrapolation to zero time being therefore again somewhat increased. It will be seen that the initial value for the rotation in a particular solution lies between the values found for water alone, whence it must be concluded that if there is any influence in the case of fructose for these particular solvents it is only very slight. It must also be remembered, however, that the solvent influence in the case of sucrose is less than one degree, and since it has been shown above that the errors of observation may amount to three degrees, it is clear that the method cannot discover whether there is in the case of fructose any real solvent influence or not. Two further experiments were tried, using a mixture of 25 volumes of water and 75 volumes of pyridine. In this mixture, solution of the fructose took place somewhat more slowly, so that it was only possible to begin to make observations after about six minutes, and at first sight it appeared that in this case there was a very decided solvent influence, the rotation when the first observations were made being already quite low and altering comparatively little with further lapse of time. When the results are plotted, however, it appears that even at 0° pyridine hastens the mutarotation greatly, and that on extrapolation to zero time a value for the initial specific rotation would be found not far removed from those obtained for aqueous solutions and aqueous ethyl-alcoholic solutions, but since this extrapolation has to be carried out through some forty degrees of rotation, it obviously cannot be accurate. The two separate solutions show a

similar agreement amongst themselves, as the three in water at 0°.

The result of these experiments, then, is that if there be any solvent influence in the case of fructose it is certainly only slight.

In regard to the results in water at 14·3° and in water–ethyl alcohol at 15·3° it ought to be noticed that the curves cut one another twice, and this may perhaps point to a difference of solvent influence, but, of course, it might indicate a temperature effect, since the same kind of argument applies to both. In the present case it may just be noted that, for example, the curves for water–ethyl alcohol (50 : 50) cut across the curve for water–ethyl alcohol (25 : 75) at 0° in quite a decided manner, the extrapolated values differing by some five degrees for the initial rotation. This is perhaps a little, but certainly not much, greater than the probable error for a single solution. Nevertheless, the result does point, although not quite definitely, to the conclusion that pure fructose, at the moment of solution in a mixture of water–ethyl alcohol (50 : 50) at 15·3°, has a slightly different rotation from fructose at the moment of solution in water–ethyl alcohol (25 : 75), at a temperature of 0°, and in this connexion it may just also be recalled that Hudson (*loc. cit.*, p. 80) draws the conclusion "that the temperature-coefficient of the rotation of stable solutions of the mutarotating sugars is not a trustworthy indication of the change in the equilibrium of the mutarotation reaction with temperature," a fact which appears to point clearly in the same direction, and to be opposed to Armstrong and Walker's assumption that change of temperature alters nothing but the equilibrium between the two forms present, showing rather that the rotations of both constituents of the solution are probably affected by the temperature change.

From the experiments just quoted it appears that the addition of alcohol retards the mutarotatory reaction in the case of fructose, as is, of course, already known, whereas the addition of pyridine accelerates it, whilst both alcohol and pyridine appear to move the position of equilibrium in the direction of the hitherto unisolated form. The experiments must, however, be regarded as inconclusive so far as they apply to the point which they were intended to elucidate.

In a paper published since these experiments were carried out, Mackenzie and Ghosh (*Proc. Roy. Soc. Edin.*, 1915, **35**, 22) have described some work on the mutarotation of various sugars in aqueous solution and in formamide solution. As regards fructose, however, they only use formamide, and compare their results with one by Parcus and Tollens for fructose in water (*Annalen*, 1890, **257**, 166). They appear to conclude that the initial rotation in

aqueous solution is about −110°, which from the experiments described above is probably much too low, whereas in formamide solution it would be about −151°. Some of the data they obtained are tabulated below. It will be observed that in most cases a

TABLE I.*

Active compound.	*t.*	*c.*	$[\alpha]_D$. Initial.	Final.
In Water.				
β-*l*-Arabinose	12·0°	2·606	+186·0°	+105·91°
l-Xylose	20·0	2·7184	+90·0	+19·3
α-*d*-Glucose	20·0	9·097	+108·0	+52·23
α-*d*-Galactose	12·5	2·1752	+139·0	+79·3
d-Mannose	20·0	2·8128	−20·0	+14·4
d-Fructose	[20·0	9·9870	*ca* −110·0	−92·09]†
α-Lactose	14·0	2·3164	+85·0	+55·25
β-Lactose	17·0	2·752	+36·0	+55·23
In Formamide.				
β-*l*-Arabinose	13·0°	2·3984	+189·0°	+116·32°
l-Xylose	20·0	4·0404	+109·0	+25·12
α-*d*-Glucose	20·0	2·5144	+122·5	+57·27
α-*d*-Galactose	18·0	2·0128	+155·0	+85·45
d-Mannose	20·0	2·0272	−26·0	+11·84
d-Fructose	20·0	2·2600	−151·0	−109·51
α-Lactose	15·0	2·2756	+83·0	+51·19
β-Lactose	17·0	1·8544	+29·5	+51·22

* Mackenzie and Ghosh (*loc. cit.*). † Parcus and Tollens (*loc. cit.*).

decided difference was found for the initial rotation in these two solvents. Thus in the case of *l*-xylose there is a difference of 19°, for α-*d*-glucose one of 14·5°, in the case of *d*-mannose one of 6°, whilst a difference between the initial rotation in these two solvents was found both for the α- and β-varieties of lactose, and this, if it could be thoroughly substantiated, would be a particularly interesting result. It will, however, be noticed that the differences recorded are in both cases, and particularly in that of α-lactose, only small, and it must be admitted that in experiments such as these where solids have to be dissolved and then brought to a definite temperature, and especially where the mutarotatory changes are rapid, the extrapolation of the rotation values to zero time is by no means easy, so that considerable errors might readily occur. It is very satisfactory, therefore, in regard to the problem now in hand, that other evidence from an entirely unimpeachable source, and evidence of a conclusive character, is available.

In a paper to which we owe our modern notions of mutarotation and, largely, the present explanation of the behaviour of the sugars, Lowry (T., 1899, **75**, 215) has shown that the rotation of normal nitrocamphor alters in 5 per cent. benzene solution from an initial value of $[\alpha]_D$ −125° to a final value of −104°, whereas in a 5 per

cent. xylene solution the rotation is initially $-99°$, and changes to $-75°$, the period of change in these two cases being about the same, namely, four days, although there is a slight difference in the temperature. In a 5 per cent. solution in chloroform the initial rotation is $-27°$, about 100° higher than in benzene, and it changes to $-15°$ in the course of a week at a temperature of 13°. Now it is particularly to be noticed here that the initial rotation in the case of xylene is greater, not merely than the initial, but even than the final rotation in the case of benzene, and, further, that the initial rotation in the case of chloroform is very much greater than the final rotation in the case of xylene, and since the rate of change is slow, making the measurements trustworthy, there can scarcely be the slightest chance that the differences in these initial values are due to errors of extrapolation, wherefore these data in point of decisiveness leave nothing to be desired. It is quite clear that α-nitrocamphor shows a very decided solvent influence, which, with absolute certainty, has nothing whatever to do with dynamic isomerism. Further, it may be remarked that the initial value for a 5 per cent. benzene solution is $-124°$, the initial value for a 10 per cent. benzene solution is $-116°$, and that for a 20 per cent. solution is $-100°$. It is evident that from these data a curve could be drawn showing the influence of concentration in benzene solution on the rotation of normal nitrocamphor—a curve uncomplicated by any question of dynamic isomerism, thus bringing normal nitrocamphor completely into line with ethyl tartrate, and there being no mutarotation influencing the former there is obviously no reason why it should influence the latter either. We have here, then, change of rotation both with change of solvent and change of concentration in a compound subject to mutarotation, but, nevertheless, quite distinct from that phenomenon. Lowry himself says in his paper that these initial specific rotatory powers represent "the effect of the different solvents on the specific rotatory power of normal nitrocamphor" (*loc. cit.*, p. 215).

There can thus be no doubt that in the case of nitrocamphor it is easy to separate quite distinctly from each other the true solvent influence and the mutarotatory effect, and it would be very difficult indeed to explain away, or minimise, the importance of this fact. Further, this being found so definitely in the case of nitrocamphor, it can scarcely be doubted that the same applies also to fructose and other mutarotatory substances, and if this does not completely undermine the mutarotatory hypothesis of Armstrong and Walker, it certainly goes a very long way towards doing so. Further data in regard to the behaviour of nitrocamphor and for hydroxy-

methylenecamphor in this connexion are given in a paper by Lowry and Courtman (T., 1913, **103**, 1217).* In both cases it is perfectly clear that solvent influence exists altogether apart from dynamic isomerism. Enough has thus doubtless been said to prove quite conclusively that what is ordinarily termed solvent influence cannot be explained as due to dynamic isomerism, since the two phenomena can exist quite independently of each other, and that, therefore, Armstrong and Walker's theory is untenable. It might also be pointed out that in the case of nitrocamphor the solvent influence free from the effects of mutarotation cannot by any possibility be regarded as small, extending as it does over some 124°, and since this is much greater than that which has been observed in the same solvents for ethyl tartrate, the mere fact that solvent effect and temperature influence in the case of this ester are large cannot be regarded as pointing in any way to the existence of dynamic isomerism in the compound.

Another point which bears in a very direct manner on this question is the following. It has been shown in a good many cases now, that, on heating, the rotation of an active substance may increase to reach a maximum value and then diminish again on further heating. This occurs for many homogeneous substances, and it occurs also for their solutions. It seems impossible that this behaviour could be explained by the assumption that the influence of temperature change is merely to alter the equilibrium between two dynamic isomerides, one of which has a low rotation and the other a high rotation. A maximum could hardly be accounted for in this way, and it need scarcely be pointed out that if the suggestion, in favour of which strong evidence has been brought forward in the first of these three papers, be true, namely, that the change of rotation of an active substance with alteration of temperature is periodic—that there may be in the temperature-rotation curve, sufficiently extended, several maximum and minimum values—Armstrong and Walker's views become less and less in accordance with the facts.

* It is to be regretted that the actual experimental data obtained by the authors in these two papers are not quoted in full, as this renders it impossible for any reader to utilise the data obtained, and might quite possibly, at some future time, involve a repetition of the whole research.

Mutarotation of Fructose in Water.

$t=14{\cdot}3°$; $c=9{\cdot}942$; half shadow angle, 1°.

Time (mins.)	$a_g^{14{\cdot}3}$ (153·5 mm.).	$[a]_g^{14{\cdot}3}$.	$\frac{1}{t_2-t_1}\log\frac{[a]_{t_1}-[a]_\infty}{[a]_{t_2}-[a]_\infty}$.
2·17	−22·63	−148·3	—
3·5	21·665	142·0	0·070
4·5	21·085	138·2	0·067
5·58	20·560	134·7	0·067
6·43	20·20	132·4	0·067
8·58	19·47	127·6	0·068
9·67	19·23	126·0	0·055
10·5	19·04	124·8	0·071
11·5	18·835	123·4	0·063
12·83	18·64	122·1	0·061
14·0	18·49	121·2	0·074
15·47	18·31	120·0	0·074
17·5	18·15	118·9	0·058
18·83	18·06	118·3	0·068
20·0	18·0	117·9	0·042
21·33	17·94	117·5	0·068
22·67	17·89	117·2	0·061
24·25	17·84	116·9	0·064
42·25	17·66	115·7	—
63·50	17·65	115·7	—

Mutarotation of Fructose in Water+Ethyl Alcohol (equal parts by volume, $d_4^{14°}=0{\cdot}930$).

$t=15{\cdot}3°$; $c=10{\cdot}056$; half shadow angle, 3°.

Time (mins.).	$a_g^{15{\cdot}3}$ (153·5 min.).	$[a]_g^{15{\cdot}3}$.	$\frac{1}{t_2-t_1}\log\frac{[a]_{t_1}-[a]_\infty}{[a]t_2-[a]_\infty}$.
5·0	−21·89	−141·8	—
6·07	21·48	139·1	0·025
7·25	21·16	137·1	0·025
8·07	20·89	135·3	0·024
8·75	20·68	134·0	0·022
9·88	20·32	131·6	0·025
10·95	20·04	129·8	0·021
12·17	19·81	128·3	0·016
13·75	19·38	125·6	0·024
14·93	19·15	124·1	0·019
16·67	18·80	121·8	0·022
17·25	18·70	121·1	0·021
18·63	18·45	119·5	0·021
19·87	18·26	118·3	0·019
21·47	18·00	116·6	0·022
22·75	17·79	115·2	0·024
32·0	16·75	108·5	0·021
∞	14·88	96·4	—

Mutarotation of Fructose in Water.

$t=0°$; $c=4·996$.

Time (mins.).	$\alpha_g^{0°}$ (150 mm.).	$[\alpha]_g^{0°}$.	$\frac{1}{t_2-t_1}\log\frac{[\alpha]_{t_1}-[\alpha]_\infty}{[\alpha]_{t_2}-[\alpha]_\infty}$.
2·67	−11·24	−150·0	—
3·42	11·185	149·3	0·018
4·40	11·13	148·5	—
5·50	11·06	147·6	0·014
6·38	10·995	146·7	—
7·18	10·975	146·4	—
8·55	10·855	144·8	—
9·40	10·84	144·6	—
10·55	10·775	143·8	—
12·72	10·66	142·3	—
14·42	10·58	141·2	—
16·12	10·50	140·1	—
18·05	10·43	139·2	—
19·48	10·35	138·1	—
∞	9·265	123·6	—

Mutarotation of Fructose in Water.

$t=0°$; $c=4·932$; half shadow angle, 1°.

Time (mins.).	$\alpha_g^{0°}$ (153·5 mm.)	$[\alpha]_g^{0°}$.	$\frac{1}{t_2-t_1}\log\frac{[\alpha]_{t_1}-[\alpha]_\infty}{[\alpha]_{t_2}-[\alpha]_\infty}$.
5·13	−11·24	−148·5	—
6·08	11·155	147·4	0·019
7·33	11·050	146·7	0·021
8·40	10·985	145·1	0·021
10·28	10·845	143·3	0·015
11·23	10·785	142·5	0·020
12·47	10·725	141·7	0·019
13·63	10·655	140·8	0·015
15·00	10·590	139·9	0·019
19·38	10·385	137·2	0·015
20·78	10·325	136·4	0·018
22·27	10·265	135·6	0·019
23·48	10·220	135·0	0·017
25·83	10·080	133·0	0·019
57·08	9·605	126·9	—
86·50	9·445	124·8	—
∞	9·345	123·4	—

Mutarotation of Fructose in Water.

$t=0°$; $c=4·928$; half shadow angle, 1°.

Time (mins.).	$\alpha_g^{0°}$ (150 mm.)	$[\alpha]_g^{0°}$.	$\frac{1}{t_2-t_1}\log\frac{[\alpha]t_1-[\alpha]_\infty}{[\alpha]t_2-[\alpha]_\infty}$.
4·58	−11·14	−150·7	—
5·50	11·09	150·1	0·015
6·22	11·03	149·2	—
6·92	10·98	148·5	0·015
8·20	10·91	147·6	—
9·20	10·84	146·6	0·014
10·25	10·795	146·0	—
11·28	10·720	145·0	0·014
13·78	10·59	143·3	—
15·67	10·50	142·1	—
17·40	10·43	141·1	—
19·92	10·32	139·6	—
42·0	9·725	131·6	—
65·0	9·41	127·3	—
∞	9·14	123·7	—

Mutarotation of Fructose in Water (25 volumes) + *Ethyl Alcohol* (75 volumes) ($d_4^{15}=0·876$).

$t=0°$; $c=4·940$.

Time (mins.).	$\alpha_g^{0°}$ (150 mm.).	$[\alpha]_g^{0°}$.
2·75	−11·360	−153·3
4·17	11·335	153·0
5·58	11·305	152·6
7·07	11·275	152·2
8·80	11·255	151·9
10·23	11·210	151·3
11·93	11·190	151·0
14·00	11·135	150·3
16·08	11·100	149·8
19·03	11·04	149·0
21·15	11·005	148·5
43·50	10·59	142·9
49·28	10·495	141·6
85·20	9·94	134·2
292·0	9·73	131·3
470·0	8·135	109·8
∞	7·05	96·1

Mutarotation of Fructose in Pyridine (75 volumes) + *Water* (25 volumes) ($d_4^{16}=1{\cdot}008$).
$t=0°$; $c=5{\cdot}019$.

Time (mins.).	$\alpha_g^{0°}$ (150 mm.).	$[\alpha]_g^{0°}$.
5·33	−8·32	−112·9
9·83	7·37	100·0
11·52	7·13	96·7
13·25	6·93	94·0
15·25	6·76	91·7
17·66	6·60	89·5
19·47	6·50	88·2
22·05	6·39	86·7
24·58	6·31	85·6
27·37	6·235	84·6
41·58	6·10	82·7
53·92	6·08	82·5

Mutarotation of Fructose in Pyridine (75 volumes) + *Water* (25 volumes) ($d_4^{16}=1{\cdot}008$).
$t=0°$; $c=4{\cdot}978$.

Time (mins.).	$\alpha_g^{0°}$ (150 mm.).	$[\alpha]_g^{0°}$.
6·52	−8·54	−114·4°
7·23	8·38	112·2
7·83	8·17	109·4
8·53	8·06	108·0
9·15	7·91	105·9
9·82	7·78	104·2
10·58	7·67	102·7
11·5	7·53	100·7
12·17	7·40	99·1
13·33	7·28	97·5
14·2	7·19	96·3
14·8	7·12	95·4
15·68	7·05	94·3

The author's thanks are due to the Carnegie Trustees for the Universities of Scotland and to the Government Grant Committee of the Royal Society for funds wherewith was purchased most of the apparatus used in the researches described in this and the two preceding papers.

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[*Received, August 17th*, 1916.]

LXXXVII.—*A Period of Induction in the Dehydration of Some Crystalline Hydrates.*

By William Norman Rae.

It has been previously observed (Cumming, T., 1910, **97**, 593; compare Partington, T., 1911, **99**, 466) that when certain crystalline hydrates are placed in a desiccator over sulphuric acid, loss of the combined water does not take place immediately; there is first a period during which the weight remains constant, and this is followed by a period in which loss of weight occurs more or less rapidly. The present paper records an attempt to investigate the question. Copper sulphate pentahydrate shows the effect very well, and was adopted as the most convenient substance for most of the experiments. The material used was some of Kahlbaum's 'for analysis,' and was not further purified; the purity appears to be of no importance, since the ordinary commercial sulphate when washed and dried, gave the same results as the purer substance.

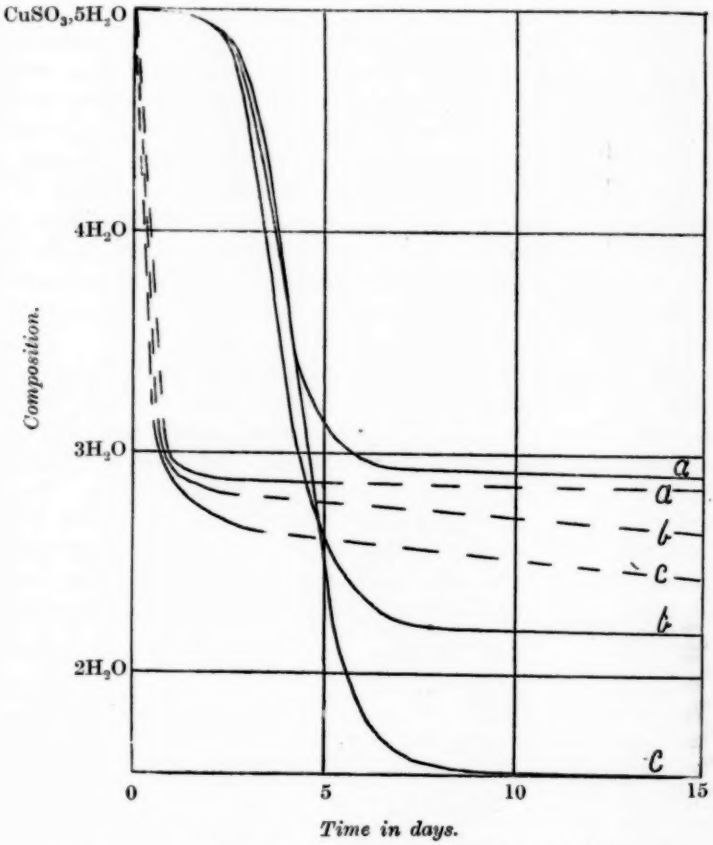
The effect of grinding to a fine powder was first tried, and three specimens were prepared. One consisted of small crystals about 0·3 cm. long; the second was a powder which passed through the 30-mesh sieve, but not through the 60-mesh, whilst the third was a powder fine enough to pass through the 90-mesh sieve. Two grams of each specimen were weighed out on to a watch-glass, and each was placed in a separate desiccator over sulphuric acid and weighed at intervals; the desiccators were all of the same size, and the same quantity of acid (100 c.c.) was used in each; the results were as follows:

Time in days.	2-Gram samples, 90-mesh powder, small crystals.		30-Mesh powder.		Small crystals, 90-mesh powder,	
	Total wt.	Loss.	Total wt.	Loss.	Total wt.	Loss.
0·0	15·338	0·000	15·112	0·000	15·058	0·000
0·75	15·337	0·001	15·110	0·002	15·058	0·000
1·75	15·333	0·005	15·107	0·005	15·057	0·001
3·75	15·145	0·193	14·869	0·243	14·864	0·194
6·75	14·880	0·458	14·729	0·383	14·758	0·300
10·75	14·842	0·496	14·701	0·411	15·744	0·314
31·75	14·814	0·524	14·660	0·452	14·740	0·318

The loss of weight is plotted against time in Fig. 1. Two points are noteworthy: first, that the induction period occurred in all three cases and lasted about two days, and secondly, that the two powders lost considerably more than two molecules of water before the rate of loss slowed down, the finest powder losing most. The experiment was repeated with similar results.

The three partly dehydrated specimens obtained in the last experiment were allowed to remain in the open air until they were completely rehydrated (shown by the weight), and were then again desiccated, weighing at intervals; the results are shown by the dotted curves in Fig. 1. The period of induction is seen

FIG. 1.



Full curves: *a, small crystals; b, coarse powders; c, fine powders.*
Broken curves: *the same after rehydration.*

to be absent, and the point of inflection in all the curves occurs at the point representing the loss of two molecules of water. The effect of stirring during the dehydration was tried by placing 6-gram samples in a wide weighing bottle standing in the centre of a desiccator; the stirrer consisted of a stout piece of platinum wire bent into an appropriate form and sealed into a glass rod

which passed through a hole in a cork in the centre of the desiccator lid, and the stirrer was rotated by means of a motor and gearing at a rate of about 1 revolution per minute. Four trials were made with similar results; the period of induction was found to be absent or is only represented by a slight convexity of the curve, and the slowing down of the rate of dehydration occurs at the correct point.

The effect of inoculation was next tried; two similar specimens were weighed out; one was touched with a hot platinum wire, causing visible dehydration at the point of contact; a similar period of induction occurred in each case.

Inoculation with 0·2 per cent. of the monohydrate had little effect, the induction period lasting thirty-six hours; with 0·25 per cent. of trihydrate this period lasted two days, whilst the addition of 1 per cent. of the trihydrate reduced it to an hour or two. The actual results in the last three cases are shown in the following table:

Effect of Inoculation on 2-Gram Samples.

Time in hours.	0·2 Per cent. of monohydrate added.		0·25 Per cent. of trihydrate added.		1·0 Per cent. of trihydrate added.	
	Weight.	Loss.	Weight.	Loss.	Weight.	Loss.
0	15·117	0·00	13·15	0·00	13·15	0·00
4	15·117	0·00	13·15	0·00	13·15	0·00
24	15·110	0·01	13·12	0·03	13·00	0·15
48	14·95	0·17	—	—	12·89	0·26
70	—	—	12·86	0·29	12·87	0·28

The addition of 2 per cent. of a specimen which had been dehydrated once and then allowed to rehydrate in the air also caused loss of water to commence at once.

The period of induction was very considerably increased in the following four experiments. In the first, copper sulphate was dissolved in a hot 1 per cent. solution of gum arabic, the solution being filtered and allowed to cool; the rate of deposition of the solid appeared to be considerably lowered by the presence of the gum; the crystals were separated, allowed to dry in the air, and then desiccated in the usual way; the induction period lasted six days, and the maximum rate of loss was not reached until about ten days from the start.

In a second experiment the ordinary powdered solid was kept in a desiccator for twenty-eight days over 54 per cent. sulphuric acid without undergoing any detectable change in weight.

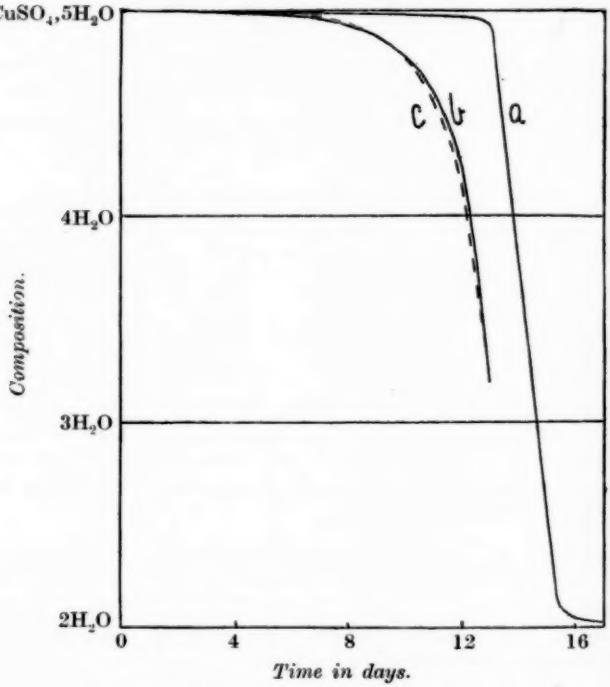
The vapour pressure of the copper sulphate is 10·90 mm. at 30·2°, whilst that of the acid calculated from Regnault's results as given in Landolt-Börnstein's tables is 9·195 at the same tem-

perature, which is also close to the ordinary temperature at the time of the experiment; the acid was analysed volumetrically at the end of the experiment.

In another experiment the desiccator containing the copper sulphate over concentrated acid was kept in the ice-box for five days without any loss of weight; the desiccation was then continued at the ordinary temperature; the results are shown in Fig. 2*a*. The weighings were made to the fourth place of decimals,

FIG. 2.

Dehydration of copper sulphate.



NOTE.—Vertical scale of *b* and *c* is 25 times that of *a*.

and the first certain loss was detected on the seventh day; the rate increased slowly at first and then more rapidly, finally slowing down when the composition of the solid reached $CuSO_4,2{\cdot}1H_2O$; this was confirmed by the analysis of the residue, which showed a loss on heating to the anhydrous salt, corresponding with 2·114 molecules of water. The rest of the residue was allowed to rehydrate in the air; then on again desiccating there was no period of induction, and the bend in the curve corresponded with the

composition of the trihydrate. The acid used in this experiment was analysed at the end, and was found to be 86 per cent., which from Regnault's results (*loc. cit.*) has a vapour pressure of 0·02 cm. at 30·2°. In the fourth experiment the pentahydrate was desiccated over about 200 grams of the monohydrate; for nine days there was no loss; after twenty-two days there was a decrease of 0·0017 in a 2-gram specimen, and five or six nuclei were visible; the monohydrate used as desiccating agent was then analysed, and found to have the composition $CuSO_4,1{\cdot}12H_2O$.

The dehydration–time curves obtained in these cases showed such a gradual increase in the rate of loss that it was thought possible to find an equation to the curves; this is found to be the case by considering the reaction to be a unimolecular one, in which the rate of loss of water is proportional to the weight of trihydrate present; or since the latter is proportional to the total loss of weight which has occurred up to the given instant, if we call the loss of weight x at the time t, we have $dx/dt = K \,.\, x$, where K is a constant; from this, $K = 1/t_2 - t_1 \,.\, \log x_2/x_1$.

The experimental results in the case, already mentioned, of the dehydration of copper sulphate pentahydrate over 86 per cent. sulphuric acid were as follows:

Weight of watch-glass = 13·34 grams.

Time in days.	Weight.	Loss = x.	Log x.	K.	Calculated loss $K = 0{\cdot}30$.
0—7	15·3251	0·0000	—	—	0·0002
8	15·3247	0·0004	$\bar{4}{\cdot}602$	—	0·0003
9	15·3244	0·0007	$\bar{4}{\cdot}845$	0·24	0·0007
10	15·3238	0·0013	$\bar{3}{\cdot}114$	0·27	0·0013
11	15·3327	0·0024	$\bar{3}{\cdot}380$	0·27	0·0026
12	15·3207	0·0044	$\bar{3}{\cdot}644$	0·26	0·0052
13	15·3147	0·0104	$\bar{2}{\cdot}017$	0·37	0·0104
14	15·140	0·185	—	—	—
15	14·980	0·345	—	—	—
16	14·900	0·425	—	—	—
17	14·895	0·430	—	—	—

These are the results shown in Fig. 2*a*, whilst the initial period is shown in Fig. 2*b* with the loss of weight on a scale twenty-five times that in the former case.

The value of the constant, and also of the loss of weight on the assumption that the value of K is 0·30, are calculated and shown.

The calculated values are plotted in Fig. 2*c*. Since the temperature was not maintained constant, the values of K would not be expected to show constancy to a very high degree of accuracy, but it will be seen from the curves that the calculated values of the losses agree quite well with those determined experimentally. Thermograph records showed that for the period of the experiment

described above, the difference between the maximum and minimum temperature was less than 4·5°, so that in reality the temperature variations were small. In the case of the crystals which were deposited from the solution in the salt in 1 per cent. gum arabic, similar results were obtained; they are shown below.

Weight of watch-glass = 13·74 grams.

Time in days.	Weight.	Loss of wt. = x.	Log x.	K.	Calculated loss $K = 0{\cdot}30$.
0	15·7426	0·000	—	—	—
5	15·7400	0·003	$\bar{3}{\cdot}477$	0·24	0·004
6	15·737	0·006	$\bar{3}{\cdot}778$	0·30	0·007
7	15·727	0·016	$\bar{2}{\cdot}204$	0·43	0·015
8	15·709	0·034	$\bar{2}{\cdot}532$	0·33	0·030
9	15·686	0·057	$\bar{2}{\cdot}756$	0·22	0·059
10	15·625	0·118	$\bar{1}{\cdot}072$	0·32	0·118
12	15·525	0·218	$\bar{1}$ 339	—	—
13	15·480	0·263	—	—	—
16	15·456	0·287	—	—	=

The rate of loss slows down at the composition $CuSO_4,3H_2O$.

Some trials were made with other substances to see if the effect is general. Each substance was crystallised once before use; it was then dried in the air, and 2 grams were weighed out and desiccated in the ordinary way.

Barium chloride dihydrate passed to the monohydrate in two days with a short period of induction.

In copper potassium sulphate the effect was well marked in the passage from $CuSO_4,K_2SO_4,6H_2O$ to the trihydrate, and was absent when stirring was employed.

The heptahydrates of magnesium, zinc, and ferrous sulphates showed no period of induction at this temperature, possibly owing to their vapour pressures being rather higher than in the other cases.

The results obtained in the experiments recorded above recall the behaviour of supersaturated solutions; in the case of such a solution, mechanical agitation or inoculation with small particles of the new phase are well known to be very favourable to the formation of the latter; with copper sulphate, stirring and also inoculation with the trihydrate are found to accelerate the dehydration to a large extent (the amount of the new phase required for inoculation is found to be larger in this case than with supersaturated solutions, where a mere trace is generally sufficient; this might be expected from the results shown in Fig. 2, and also from the fact that we are dealing with a solid. It is well known that the solubility of a substance is influenced by the state of division of the solid phase; if this is very finely divided, the solubility is

greater than if it consists of coarser particles; this fact is probably connected with the phenomenon of supersaturation.

Pavlov (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 679) states that very small particles of some organic solids, when placed in the same space with larger granules of the same solid, tend to disappear, whilst the larger granules increase in size; so that it appears that very small particles of a solid have a higher vapour pressure than larger ones, in the same way as small drops of water have a higher vapour pressure than larger ones; the latter effect explains the difficulty of forming, or rather starting the formation of, a cloud in the absence of suitable nuclei, although the vapour pressure may be much greater than the saturation pressure at the same temperature.,

It may well be, that the vapour pressure of very small particles of copper sulphate trihydrate may be much greater than that of larger particles, and may approach that of the pentahydrate; if this is really the case, it is clear that the formation of these particles, and therefore the initial stages of the change from pentahydrate to trihydrate, will take place with great difficulty until the particles of the latter have reached a certain size. When the dehydrated substance is rehydrated for as long as a month there are still left sufficient nuclei of the trihydrate to prevent the induction period from occurring. It appears from the results that the rate of the reaction at the beginning is proportional to the amount of trihydrate present at any time and this points to the fact that it is to the vapour pressure of this substance that we must look for the cause of the effects observed.

Partington (*loc. cit.*) in his experiments on the determination of the vapour pressure of crystalline hydrates, was obviously dealing with the same effect as that considered here; he, however, interprets his results as showing that the vapour pressure at the commencement of the dehydration is lower than later on, and suggests the intermediate formation of an amorphous, lower hydrate, which ultimately changes to a more stable, crystalline form; the postulation of such a compound seems to be unnecessary. No satisfactory explanation can be advanced for the cases in which the dehydration proceeds to a greater extent than would be expected before the speed slows down; it was noticeable that in general (but not always) the period of induction was connected with the overshooting of the mark; this is shown in Fig. 2, where a long period of induction is accompanied by a large loss before the curve bends; when the substance was stirred, both the period of induction and the overshooting were absent; the latter effect is also usually greater the more finely divided the powder.

It was thought possible that in such cases the system was never in equilibrium, but that the process of dehydration was so slow that the acid had plenty of time to remove water and so keep the pressure down below that of the monohydrate, so that immediately any trihydrate was formed it would be able to commence decomposition into the monohydrate; the three hydrates would then be present at the same time, but not in equilibrium, since the two higher would both be decomposing; such a state is conceivable in the circumstances.

In the present case such an explanation does not suffice to explain all the results; thus, the most rapid rate of transformation from trihydrate to monohydrate observed in any of the experiments was a loss of 10 per cent. in fifty days at the ordinary temperature, that is, a loss of 0·2 per cent. per day; in the case shown in Fig. 2 the dehydration lasted, including the period of induction, for seventeen days; an extra loss (beyond the loss of 14·4 per cent. which occurs in the transition from penta- to trihydrate) amounting to 3·4 per cent., due to the above cause, would be the greatest one would expect; the actual excess loss was twice this amount.

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[*Received, June 23rd*, 1916.]

LXXXVIII.—*Phthalonic Acid and its Derivatives.*

By JOSEPH TCHERNIAC.

PHTHALONIC acid, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, is easily obtained by the oxidation of naphthalene with manganates or permanganates (Tcherniac, D.R.-P., 79693, 86914).*

In the laboratory the preparation can be quite well carried out

* The details of preparation given in the above quoted patent specifications were not at the time fully abstracted in the chemical periodicals. The first comprehensive account appeared four years later in a paper by Graebe and Trümpy (*Ber.*, 1898, **31**, 369). The only difference between these authors' description and mine is one of figures, the relative proportions remaining exactly the same. Graebe and Trümpy use 10 parts of naphthalene, 62·5 of permanganate and 625 of water, whilst my figures were 12 parts of naphthalene, 75 of permanganate and 750 of water. They state quite correctly that they have strictly followed the details of my method. Other chemists, however, have not been so fair, and speak of Graebe and Trümpy's description without even mentioning that it is copied from my specification.

in round-bottomed glass flasks, provided they are heated in a bath * at about 115°, so as to maintain a rapid ebullition; stirring is then unnecessary, and the operation does not last more than four to five hours. Care must be taken to keep the condenser clear, as it becomes blocked by the subliming naphthalene. On a small scale it is best to concentrate the filtered solution, to acidify with sulphuric acid, and to extract with ether. The extract is evaporated to dryness and treated with a small quantity of water, when, owing to its much greater solubility, the phthalonic acid is practically alone dissolved, whilst the phthalic acid remains in the residue.

As mentioned in the specification, phthalonic acid can be obtained from water in large, compact crystals. They contain $2H_2O$, as Graebe and Trümpy have already made known.

A saturated solution at 15° has the specific gravity 1·243, and contains 64·4 per cent. of the anhydrous acid. The acid is very sparingly soluble in pure, even hot chloroform. Commercial chloroform, containing traces of alcohol, dissolves it much more readily, and can be used with advantage for extracting the crude product in the Soxhlet apparatus (of course, the alcohol esterifies a corresponding proportion of the acid). It is very readily soluble in alcohol, ether, or acetone, but sparingly so in cold or hot benzene or in light petroleum.

When titrated with methyl-orange, it behaves like a monobasic acid, but the reaction is very indistinct. With phenolphthalein the change of colour is quite sharp, and the acid is found to be dibasic. It is dibasic also with tincture of cochineal and with litmus (with the latter when titrated hot). With cochineal the indication is fairly sharp.

* As material for a bath, which I have been using with great advantage for the last thirty years, I recommend potassium thiocyanate. Owing to its ready solubility in water and the high boiling point of the saturated solution on the one hand, and the low melting point (about 160°) of the dry salt on the other, the solution passes almost imperceptibly on heating into the state of molten salt, and any temperature up to 400° and above can be easily reached and maintained. The temperature of the bath is easily kept constant by means of an ordinary stoppered cylindrical separating funnel of about 250 c.c. capacity, the perforation of the stopcock of which is of at least 8 mm. bore. When the solution of potassium thiocyanate reaches the temperature to be maintained, I bring the end of the delivery tube of the separating funnel just into contact with the surface of the thiocyanate solution, fill the funnel with distilled water, insert the stopper, and open the stopcock; the apparatus now works as a bird fountain, maintaining the level of the solution and consequently a constant temperature. When the water in the funnel requires replenishing, all that is necessary is to close the stopcock, remove the stopper, re-fill the funnel with distilled water, re-insert the stopper, and re-open the stopcock.

The reaction of phthalonic acid with permanganate is characteristic and striking enough for a lecture experiment. When sulphuric acid (50 per cent.) and permanganate solution are added to a 10 per cent. solution of phthalonic acid, the colour disappears after a minute or so, a sudden and rapid evolution of carbon dioxide takes place, and the liquid sets to a dazzling white magma of fine crystals of phthalic acid. The very voluminous precipitate shrinks gradually, the crystals becoming much denser.

The method of analysis which was used for the estimation of phthalonic acid was by titration with permanganate in acid solution (Boswell, *J. Amer. Chem. Soc.*, 1907, **29**, 230).

Phthalonic acid is an excellent material for the preparation of many interesting substances. Graebe and Trümpy (*Ber.*, 1898, **31**, 369) have shown how easy it is to obtain from phthalonic acid: phthalidecarboxylic acid, phthalide, phthalaldehydic acid, and homophthalic acid—all with good yields, and I have prepared the following further derivatives of phthalonic acid:

Phthalonic anhydride, $C_6H_4<\begin{matrix}CO\cdot CO\\ CO\cdot O\end{matrix}$, obtained by the author long ago (see *Ber.*, 1898, **31**, 139), is easily prepared by the action of acetic anhydride on phthalonic acid. Equal weights of the reagents are heated on the water-bath for an hour or two; on cooling, the mixture sets to a thick, yellow paste, which is allowed to remain for a day, and then well crushed in a mortar, filtered, washed with ether (dried over sodium), and placed in a vacuum over sulphuric acid and moistened solid sodium hydroxide until constant weight is attained. The yield is nearly theoretical. If the product is still found to retain acetic acid, it must be crushed again, washed with dry ether, etc.

The mother liquor, on keeping, deposits further small quantities of anhydride, which is white, although slightly impure.

Found: C = 61·07; H = 2·48.

$C_9H_4O_4$ requires C = 61·36; H = 2·27 per cent.

Phthalonic anhydride crystallises from acetic anhydride in white or slightly yellow needles. It is very readily soluble in boiling ethyl acetate, and is deposited therefrom on cooling in small, brilliant crystals. The ethyl acetate solution is precipitated by light petroleum. As may be seen from the method of purification, phthalonic anhydride is sparingly soluble in ordinary ether.

The anhydride, when rapidly heated, melts at 185—186° with frothing; after solidification it melts at a much lower temperature.

Phthalonic Anhydride and Ammonia. Phthalonamic Acid.

Phthalonic anhydride (8·8 grams) was added gradually to concentrated ammonia (10 c.c.) cooled with ice. The mixture was allowed to remain for a short time, and then acidified with an ice-cold mixture of concentrated hydrochloric acid (7·5 c.c.) and water (2·5 c.c.). The precipitate was collected on the following morning, washed with very little water, and dried in a vacuum, when it melted and decomposed at 135—137°.

Found: C = 55·93; H = 4·12.

$C_9H_7O_4N$ requires C = 55·95; H = 3·63 per cent.

The compound is very readily soluble in water. By slow evaporation of the cold solution it crystallises in well-developed, compact prisms melting and decomposing at 155°. The crystals do not lose their transparency in a vacuum over sulphuric acid.

Gabriel and Colman (*Ber.*, 1900, **33**, 999) have described a phthalonamic acid which they obtained by the hydrolysis of phthalonimide (from carbindigo). Their acid crystallises with $1\frac{1}{2}H_2O$, and when anhydrous melts and decomposes at 178—179°. It is converted by alkali hypochlorite into isatic acid, which shows it to have the constituton $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$. It differs, therefore, from the phthalonamic acid described above, which evidently has the constitution $NH_2{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$. In accordance with this formula, it yields no isatin with alkaline hypochlorite.

Neither is the phthalonamic acid from phthalonic anhydride identical with the dibasic acid, $C_9H_7O_4N$, prepared by Graebe and Trümpy (*loc. cit.*, p. 371) from phthalonic acid and ammonia, which they consider as probably possessing the constitution

$$CO_2H{\cdot}C_6H_4{\cdot}C(:NH){\cdot}CO_2H$$

(or a polymeride). The properties of their acid are quite different from those of the author.

The action of alcohols on phthalonic anhydride is being investigated.

Phthalonic Acid and Potassium Cyanide. Amide of Phthalidecarboxylic Acid.

Phthalonic acid (194 grams: 1 mol.), a solution of potassium hydroxide (112·2 grams: 2 mols.), and a solution of potassium cyanide (65 grams: 1 mol.) were mixed and diluted with water to 4 litres in a large flask closed by an india-rubber stopper carrying two tubes, the one, which reached near the surface of the liquid, being in connexion with a carbon dioxide generating apparatus, and the

other—the outlet—being fitted with a pinch-cock, by which it could be closed. When all the air above the mixture had been displaced by carbon dioxide, the outlet tube was closed, whilst the inlet tube remained in connexion with the carbon dioxide apparatus. Before reaching the flask the carbon dioxide passed through a wash-bottle containing water, which served the double purpose of washing the gas and indicating the speed of its absorption. The flask was shaken from time to time until the absorption of carbon dioxide—as shown by the cessation of bubbles in the wash-bottle—was complete. The quantity of carbon dioxide absorbed was 110 grams. An abundant, yellow precipitate was gradually formed. After six days, when traces of a red deposit began to appear, the precipitate was collected, crushed, and dried (117 grams). It was then crystallised from hot water, washed, and dried. The substance (105 grams) was quite colourless, and melted at 185·5°.

Found: C = 60·87; H = 4·24; N = 7·91.

$C_9H_7O_3N$ requires C = 61·02; H = 3·95; N = 7·91 per cent.

The substance is sparingly soluble in cold water or alcohol, more readily so in boiling water (for its solubility in water, see later) or methyl alcohol. It dissolves almost completely in potassium hydroxide solution, completely in ammonia.

When distilled with twenty times its weight of zinc dust, it yields, amongst other products, an oily base the picrate of which has the properties of *iso*quinoline picrate. It crystallises in small, brilliant yellow needles melting at 220·5°, and is sparingly soluble in water.

One gram of the substance, $C_9H_7O_3N$, was boiled with 12 c.c. of potassium hydroxide solution (1 c.c. = 0·08 gram KOH) for one and a-half hours under a reflux condenser. The solution, which was red at first, became colourless after boiling for three-quarters of an hour. After cooling, 3 grams of 50 per cent. sulphuric acid were added, when an oily substance separated and soon solidified (0·9862 gram when dry). It was crystallised from 10 grams of boiling water (0·715 gram), and then melted at 151°, the melting point of phthalidecarboxylic acid, all the other properties of which it possessed. (Found, C = 60·89; H = 3·39. $C_9H_6O_4$ requires C = 60·67; H = 3·37 per cent.)

It was evident, therefore, that the product of the reaction of nascent hydrogen cyanide with alkaline phthalonate was the amide of phthalidecarboxylic acid, which, by hydrolysis, had given the acid, as was to be expected:

$$C_6H_4\begin{<}\begin{matrix}CH(CO\cdot NH_2)\\ \text{———}CO\text{———}\end{matrix}\end{>}O + H_2O = C_6H_4\begin{<}\begin{matrix}CH(CO_2H)\\ \text{———}CO\text{———}\end{matrix}\end{>}O + NH_3.$$

In order to make the matter doubly sure, the amide was prepared directly from phthalidecarboxylic acid.

The acid (5·096 grams) was heated with phosphorus pentachloride (5·9715 grams) for one hour in the water-bath until the evolution of gas stopped, and the phosphoryl chloride was removed by distillation in a vacuum. The residue (5·663 grams) was cooled and treated with an excess of dilute ammonia (9 per cent.). The product was yellow, and became colourless on washing with water. When dry, it weighed 2·596 grams, and after recrystallisation from 75 grams of boiling water 2·267 grams. The melting point of this substance and of that prepared from phthalonic acid, taken by attaching the capillary tubes containing the two products to one thermometer, and heating in the same bath, were found to be identical, namely, 185·5°.

A comparison of the solubilities in water at 16·2° and at the boiling point (735 mm.) gave the following results:

Parts of the substance dissolved by 100 parts of water:

From phthalonic acid.	From phthalidecarboxylic acid.	
0·133	0·132	at 16·2°
5·757	5·650	at the boiling point (735 mm.).

The differences are within the limits of experimental error.

There can be no doubt, therefore, that the substance, $C_9H_7O_3N$, from phthalonic acid is identical with the amide of phthalidecarboxylic acid.

Phthalonic Acid and Sulphur Dioxide.

Graebe and Trümpy (*loc. cit.*, p. 375) have shown that phthalaldehydic acid can be obtained with a satisfactory yield by evaporating to dryness a solution of molecular proportions of phthalonic acid and sodium carbonate, dissolving the salt in a 40 per cent. solution of sodium hydrogen sulphite at 60°, again evaporating to dryness, acidifying, and extracting with ether. On slightly modifying the conditions, an entirely different product is obtained; for example, when sodium phthalonate is dissolved in water and heated with an excess of sodium hydrogen sulphite solution, evolution of carbon dioxide begins at about 70°, and continues on boiling until nearly one molecule of carbon dioxide is evolved from one molecule of phthalonic acid. When the solution is evaporated to dryness and the residue redissolved in water with the addition of an excess of concentrated hydrochloric acid, again evaporated to dryness in the water-bath, heated for some time at 110°, and the residue extracted with ether, small quantities of substances are obtained—

apart from a little phthalaldehydic acid—which are different from the latter, and also differ with apparently slight variations of the conditions. In one preparation small, yellow needles were obtained, which, after crystallisation from toluene, melted at 232° and were insoluble in water. Analysis gave the following results:

Found: C = 67·80; H = 3·91.

$C_{16}H_{10}O_5$ requires C = 68·08; H = 3·54 per cent.

The chief product in all cases, however, is insoluble in ether, and proves to be a very stable organic sodium salt which, as appears from the conditions of its formation, withstands heating with concentrated hydrochloric acid without sensible decomposition.

Later it was found that the use of hydrochloric acid was not necessary for the production of the salt; it was therefore dispensed with in the following method of preparation.

A solution of phthalonic acid (200 c.c. of 2*N*-solution = 38·8 grams) and aqueous sodium hydroxide (100 c.c. of 2*N*-solution) were heated to 80°, and sulphur dioxide (25·6 grams: 4/10 mol.) was introduced. The solution was then evaporated in the water-bath to incipient crystallisation, the crystals collected after cooling, the mother liquor again evaporated, and so on. In all, about 44 grams of the crude salt were obtained, which, when recrystallised twice from water, yielded 27·35 grams of the purified salt. For analysis, 5 grams of the purified salt were dissolved in 15 grams of hot water and the solution allowed to cool slowly. One single, well-developed, and transparent crystal was obtained, which, after having been well dried with filter paper, weighed 1·3499 grams. The crystal, on continuing the drying in a vacuum over sulphuric acid, lost 0·0875 gram (= 6·48 per cent.), and became opaque. The dry residue was used for the following determinations:

Found: C = 38·09; H = 3·06; S = 12·46; Na = 8·86.

$C_8H_7O_6SNa$ requires C = 37·79; H = 2·75; S = 12·60; Na = 9·06 per cent.

Found: H_2O = 6·48.

$C_8H_7O_6SNa,H_2O$ requires H_2O = 6·61 per cent.

When rapidly heated the crystallised salt melts and decomposes at 182°; the anhydrous salt is decomposed at 173°. The substance is readily soluble in hot water or hot alcohol, and can be purified by recrystallisation from either of these solvents.

Action of Ammonia.—The hydrated salt (5·44 grams) was dissolved in 20 c.c. of water and 4 c.c. of concentrated ammonia, and left overnight. The white needles which separated were collected, washed, and dried. They weighed 2·787 grams and melted at 169—171°, after recrystallisation from water.

Found: C = 64·61; H = 5·02; N = 9·32.

$C_8H_7O_2N$ requires C = 64·43; H = 4·70; N = 9·40 per cent.

The substance is soluble in potassium hydroxide solution, and can be reprecipitated by carbon dioxide, apparently unaltered.

There is little doubt that the substance is identical with aminophthalide, the melting point of which is given as 167°, and that it is produced as follows:

$$C_8H_7O_6SNa + NH_3 = C_6H_4\begin{<}{CH(NH_2)\atop CO}\end{>}O + NaHSO_3 + H_2O.$$

In other preparations the melting points of the crude products varied from 155° to 175°, but on purification these proved to be identical. The yield was nearly theoretical (93—95 per cent.).

The question arises as to the constitution of the salt $C_8H_7O_6SNa$. The composition is the same as that of a compound of phthalaldehydic acid with sodium hydrogen sulphite,

$$CO_2H\cdot C_6H_4\cdot CH(OH)\cdot SO_3Na,$$

but the stability towards strong mineral acids excludes this interpretation.

The idea naturally occurs that the salt may belong to that extensive group which contains the aromatic sulphonic acids, as well as the aliphatic isethionic, methanetrisulphonic, and Müller's hydroxymethane-mono- and -di-sulphonic acids, etc., all substances stable towards mineral acids and in which the sulphur is directly united with the carbon. This assumption does not seem, however, to be justified in view of the mode of formation of the salt and the facility with which the sulphur is eliminated by the action of ammonia.

From the present knowledge of the properties of the substance the following formula seems to be admissible for the crystallised salt:

$$C_6H_4\begin{<}{CH(SO_3Na)\atop CO}\end{>}O,2H_2O.$$

As has been shown, $1H_2O$ at least is held as water of crystallisation and is given off in a vacuum at the ordinary temperature; as to the mode of combination of the second molecule of water, nothing definite can be said at present.

It will be interesting to prepare the sodium hydrogen sulphite compound of phthalaldehydic acid and to compare it with this salt.

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[*Received, August* 21, 1916.]

LXXXIX.—*The Interaction of Aldehydes and Thiocarbamides in the Presence of Acids.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

A COLD aqueous solution of thiocarbamide mixed with aldehyde remains clear if the mixture is kept neutral; on acidification, a white solid is gradually deposited, having the composition $CSN_2H_2{:}CHMe$; this substance, insoluble in water and in dilute mineral acids, when boiled with the latter is hydrolysed into its components:

$$CSN_2H_2{:}CHMe + H_2O \longrightarrow CSN_2H_4 + CHMe{:}O.$$

Accompanying the primary condensation product just mentioned, there may be a secondary one, $CSN_2H_2{:}CHMe,CHMe{:}O$; it has properties mostly similar to those of the primary, but is soluble in boiling water.

The primary compound originates through the spontaneous decomposition, in the presence of water, of an unstable *iso*thiocarbamide base, $NH_2{\cdot}C(:NH){\cdot}S{\cdot}CHMe{\cdot}OH$, the 'hydrochloride' corresponding with which is producible from thiocarbamide and α-chloroethyl alcohol:

$$CSN_2H_4 + CHMeCl{\cdot}OH \longrightarrow CSN_2H_3{\cdot}CHMe{\cdot}OH,HCl.*$$

With water, the 'hydrochloride' yields an acid solution, from which, on neutralisation, the base separates as a white, amorphous solid; the latter, gradually losing its basic properties, changes at last into the insoluble condensation product. In the dilute aqueous solution of the 'hydrochloride,' too, a change is presently visible, the liquid becoming turbid, with deposition of the compound, $CSN_2H_2{:}CHMe$; the phenomenon, indeed, is predictable, for the acidity of the solution betokens hydrolysis, with consequent formation of the unstable base.

The sequence of changes is partly displayed in the following synopsis:

(1). $CHMe{:}O + HCl \longrightarrow CHMeCl{\cdot}OH$

(2). $\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S + CHMeCl{\cdot}OH \longrightarrow \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S\!<\!\begin{matrix}CHMe{\cdot}OH\\Cl\end{matrix}$

* The constitution of the so-called 'hydrochloride' (and of other like additive compounds of thiocarbamide) is not yet fully understood; it may be:

(*a*) $ClNH_3{\cdot}C(:NH){\cdot}S{\cdot}CHMe{\cdot}OH$, (*b*) $\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!CCl{\cdot}S{\cdot}CHMe{\cdot}OH$, or

(*c*) $\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>\!C{:}S\!<\!\begin{matrix}CHMe{\cdot}OH\\Cl\end{matrix}$.

In the absence of definite knowledge, we select (*c*).

(3). $\begin{matrix}NH_2\\NH_2\end{matrix}\!>\!C\!:\!S\!<\!\begin{matrix}CHMe\cdot OH\\Cl\end{matrix} \longrightarrow HCl + NH_2\cdot C(\!:\!NH)\cdot S\cdot CHMe\cdot OH$

(4). $NH_2\cdot C(\!:\!NH)\cdot S\cdot CHMe\cdot OH \longrightarrow H_2O + CSN_2H_2\!:\!CHMe.$

Later on, it will be shown that reaction (4) is accomplished in two stages.

Naturally, the composition of the base could not be checked by quantitative analysis. By introducing ethoxyl in place of hydroxyl, however, a corresponding base,

$$NH_2\cdot C(\!:\!NH)\cdot S\cdot CHMe\cdot OEt,$$

was obtained, stable enough to allow of such checking. After some days it, too, began to decompose, with the formation of the non-basic product.

The reluctance of aldehyde to condense with thiocarbamide in the presence of water is manifested equally in its absence. Yet in aqueous solutions a mere trace of any acid suffices to bring about the condensation; moreover, the presence of water is essential to its occurrence in the cold, for the aforesaid syrupy 'hydrochloride,' so long as it is kept dry, shows no sign of chemical change. Consequently, the acid does not act by "contact"; in activating the system, its power depends on its capacity to form, with one of the components, a chemical compound which attacks the other. Thus, if an acid, HX, yields CHMeX·OH, and this in turn produces with the thiocarbamide the additive compound or salt—in the presence of water, of course—the condensation process is started and will proceed to a finish.

There is, however, the possibility that, HX combining with the thiocarbamide in such a way as to transform it into *iso*thiocarbamide, $NH_2\cdot C(\!:\!NH)\cdot SH$, the latter might combine with the aldehyde to form a salt of the base, $NH_2\cdot C(\!:\!NH)\cdot S\cdot CHMe\cdot OH$. Apparently supporting this idea is the fact that solid thiocarbamide hydrochloride reacts with aldehyde, producing the same 'hydrochloride' as that yielded by thiocarbamide and α-chloroethyl alcohol. Against this, however, thiocarbamide hydrochloride, as such, is practically non-existent at *N*-concentration of the hydrochloric acid; whilst *N*/10-hydrochloric acid is a quick catalyst (ten to fifteen minutes at the ordinary temperature with about 8 per cent. of dissolved thiocarbamide). Moreover, according to E. A. Werner (T., 1912, **101**, 2185), acetic acid cannot transform thiocarbamide into *iso*thiocarbamide—a conclusion which appears to be fully justified—yet acetic acid, although not so quick as the strong mineral acids, is a good catalyst, even when present in but small proportion. In the case of thiocarbamide hydrochloride, mentioned above, the aldehyde probably (like water) withdraws from the salt the elements of hydrogen chloride, uniting then with the acid to form α-chloro-

ethyl alcohol; it is noticeable, too, that, on coming into contact with the salt, the aldehyde boils freely (it does the same when brought into contact with ordinary hydrochloric acid, the undistilled portion greedily absorbing hydrogen chloride).

In the absence of direct proof that every acid which can serve as catalyst has also the power of feeble union * with the aldehyde, the first view is attained merely by exclusion of the second. A tetra-substituted thiocarbamide, however, affords quite readily the 'hydrochloride,' $CS(NR_2)_2,CHMeO,HCl$. Here no *iso*-form can be present; the reactants, therefore, must be a thiocarbamide and α-chloroethyl alcohol. Moreover, since in this case the process runs independently of change of thiocarbamide into *iso*thiocarbamide, there is no particular reason to assume that such a change occurs in other cases.

Under the name 'secondary,' another condensation product has been mentioned above; this name implies that a second molecule of aldehyde enters into the composition of the substance—not that it is a by-product. When tartaric acid is used as catalyst, little or none of the secondary compound is formed; but when the reaction was carried out with acetone as solvent and hydrochloric acid as catalyst, the resultant solid consisted almost exclusively of $CSN_2H_2{:}CHMe,CHMeO$.

Corresponding with the latter, there is a hydrochloride, $CSN_2H_2{:}CHMe,CHMeO,HCl$.

Towards thiocarbamide, the behaviour of formaldehyde is essentially similar to that of acetaldehyde; the free base, however, changes very quickly into the condensation product, $CSN_2H_2{:}CH_2$.

Alkyl and aryl substituted thiocarbamides, when treated with hydrogen chloride in the presence of aldehydes, yield the corresponding 'hydrochlorides'; they are clear syrups, which slowly harden on keeping in a vacuum. From mono-substitution derivatives the corresponding bases and condensation products are obtained by neutralising the solutions; with diphenylthiocarbamide, however, the condensation products, being very subject to hydrolytic change, were not isolated in a pure condition. Tri- and tetra-substitution derivatives, of course, cannot yield condensation products.

From acyl substituted thiocarbamides, in the presence of aldehyde, the syrupy 'hydrochlorides' were produced, but in no case was the corresponding condensation product obtained, the bases being very readily hydrolysed. By a method not entailing the use of free acids, these compounds have in some cases been pre-

* α-Cyanoethyl alcohol (α-hydroxypropionitrile) reacts extremely slowly with aqueous thiocarbamide.

pared, namely, by the interaction of acylthiocarbimides with aldehyde–ammonia. Here, the first product, a thiocarbamide, AcNH·CS·NH·CHMe·OH, loses spontaneously the elements of water, thereby giving $CS<^{NAc}_{NH-}>CHMe$.

Constitutions of the Substances Formed in the Course of the Aldehyde–Thiocarbamide Condensation.

(1) *The 'Hydrochloride.'*—That obtained from *ab*-diphenyl-*ab*-dimethylthiocarbamide and acetaldehyde must have the constitution, $R_2N>C{:}S<^{CHMe\cdot OH}_{Cl}$ or else $R_2N>CCl\cdot S\cdot CHMe\cdot OH$. Experiments in which magnesium methyl iodide was employed, with a view to replace chlorine by methyl, led to no definite result. For reasons already discussed (Dixon and Taylor, T., 1912, **101**, 2523, etc.), we are rather in favour of the sulphonium formula, and use this, provisionally, to represent all "salts," whether substituted or not.

(2) *Bases.*—As to the constitution of these, there is no uncertainty. From a 'salt' of the above configuration the base to be expected is $NH_2\cdot C(:NH)\cdot S\cdot CHMe\cdot OH$; whether produced by the direct union of hydrogen and chlorine or through the dehydration of an unstable compound, $NH_2>C{:}S<^{CHMe\cdot OH}_{OH}$, is quite unimportant. By the isolation of the comparatively stable ethoxy-derivative, $CSN_2H_3\cdot CHMe\cdot OEt$, the composition of the corresponding hydroxy-analogue may safely be inferred as $CSN_2H_3\cdot CHMe\cdot OH$. For the rest, the well-marked basicity of both products suffices to define the constitution of the residual fraction as $\cdot S\cdot C(NH)\cdot NH_2$.

(3) *Condensation Products.*—Here, apparently, is sure ground. For, in losing the elements of a molecule of water, the *iso*thiocarbamide base would yield an *iso*thiocarbamide ring; that is, the formaldehyde and the acetaldehyde derivatives would be respectively:

$$NH{:}C<^{NH}_{S-}>CH_2 \quad \text{and} \quad NH{:}C<^{NH}_{S-}>CHMe,$$

or 2-iminotetrathiazan and 2-imino-4-methyltetrathiazan.

Clearly, this is not the case. The imino-derivative of a four-membered, heterocyclic ring, $CH_2<^{NH}_{S-}>CH_2$, if not a liquid, would at least be readily fusible; both condensation products are really infusible, but decompose (with apparent melting) at 200° or upwards. Such an imino-compound would be a base, and alkaline towards ordinary indicators; the condensation products

actually obtained are neutral towards litmus, etc., and insoluble in aqueous acids. By hydrolysis, the iminotetrathiazans should give cyanamide, together with an unstable mercaptan,

$$OH\cdot CHR\cdot SH \longrightarrow RCH{:}O + H_2S;$$

whereas, the actual products of hydrolysis are thiocarbamide and an aldehyde. In short, these compounds, the formation of which is preceded by that of an *iso*thiocarbamide base, are themselves derivatives of normal thiocarbamide. Now, an *iso*thiocarbamide ring, once formed—at all events, one of the above pattern—would certainly not change into a normal thiocarbamide ring. In connexion with such "slippery" molecules, one may well hesitate to use the word "certainly"; what is here meant is, that such a change has never yet been observed to occur. On the other hand, what has frequently been observed in cases where a base, $NH_2\cdot C(:NH)\cdot S\cdot CO\cdot R$, is liberated from its 'salt,' is the migration of the radicle, $\cdot CO\cdot R$, from sulphur to nitrogen, a derivative of normal thiocarbamide, $R\cdot CO\cdot NH\cdot CS\cdot NH_2$, thereby resulting (Dixon and Hawthorne, T., 1907, **91**, 122; Dixon and Taylor, *ibid.*, 912; 1908, **93**, 18; 1912, **101**, 2513).* Evidently, the complex, $R\cdot CH(OH)\cdot$, although much less electronegative than R·CO (R is a hydrocarbon radicle), is susceptible to a like movement, which occurs precedently to the elimination of water. In this way, the production of a neutral condensation product from the antecedent base becomes intelligible, the series of changes occurring as represented by the scheme:

$$\begin{matrix}NH_2\\NH\end{matrix}\!\!>\!C\cdot S\cdot CHR\cdot OH \longrightarrow CS\!<\!\begin{matrix}NH_2\\NH\cdot CHR\cdot OH\end{matrix} \longrightarrow$$

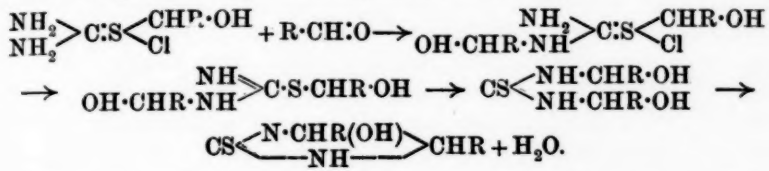
$$H_2O + CS\!<\!\begin{matrix}NH\\NH\end{matrix}\!\!>\!CHR.$$

By heating pure acetaldehyde with thiocarbamide at 100°—a method not calculated to produce an *iso*-form—Emerson Reynolds (*Reports Brit. Assoc.*, 1871, 78; *Chem. News*, 1871, **24**, 87) obtained a compound, $CSN_2H_2{:}CHMe$, the general properties of which coincide fairly with those of our condensation product. Some minor discrepancies there are; for example, his compound showed a sparing solubility in alcohol, whereas ours is nearly insoluble. As he operated with excess of acetaldehyde, however, it

* Instancing the case of *iso*thiohydantoic acid, $NH_2\cdot C(:NH)\cdot S\cdot CH_2\cdot CO_2H$, Rây and Fernandes (T., 1914, **105**, 2160) "dispose" of a conclusion by Dixon and Taylor (*loc. cit.*, p. 2515), that if X is a well marked acyl radicle, $NH_2\cdot C(:NH)\cdot SX$ is an essentially unstable molecule. In the case cited by these authors, the acid part, $\cdot CO_2H$, is separated from the S by CH_2:, many such compounds have been prepared by chemists, and are well known not to be unstable. The context shows that these were not meant.

is possible that the solid was mixed with a little of the secondary condensation product, which is somewhat soluble in alcohol.*

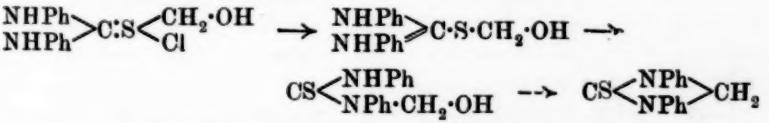
In the case of secondary 'hydrochlorides,' their formation and the subsequent changes are explicable as follows:



This explanation, however, is merely provisional, for the steps of the secondary reaction have not yet been followed experimentally in sufficient detail to warrant a decision.

As stated earlier, the properties of the thiocarbamide–formaldehyde primary condensation product are not those to be expected of 2-imino-tetrathiazan; to make certain, it was desirable to prepare the latter. Failing to obtain it from thiocarbamide and methylene di-iodide (which gave, instead, the hydriodide of methylenedi*iso*thiocarbamide, $NH_2{\cdot}C(:NH){\cdot}S{\cdot}CH_2{\cdot}S{\cdot}C(:NH){\cdot}NH_2$ —a stable, well-marked base), we sought, from thiocarbamide and *as*-dichloroethane, to procure the homologous $NH{:}C\langle{}^{NH}_{S}\rangle CHMe$; the constituents, however, failed to unite, even when heated together under pressure at 100°. An attempt to prepare, from phenylthiocarbimide and methyleneaniline, a ring compound, $CS\langle{}^{NPh}_{NPh}\rangle CH_2$, for comparison with Foerster's *iso*-base, $NPh{:}C\langle{}^{NPh}_{S}\rangle CH_2$ (*Ber.*, 1888, **21**, 1872), was also unsuccessful.

Such a compound is to be expected from the 'hydrochloride' which formaldehyde yields with thiocarbanilide:



and in the solid obtained from that hydrochloride by the elimination of hydrogen chloride the ring compound is manifestly present. It readily decomposes, however, into thiocarbanilide and formaldehyde, and we could not prepare a really pure specimen. The failures to isolate methylenediphenylthiocarbamide were not unex-

* In the earlier stages, we took the white solid to be a single substance, the analytical figures giving, sharply, the ratio $N_2 : S$. As the figures were always too low, the presence of a second compound was suspected, and ultimately the two were separated by means of boiling water.

pected, Senier and Shepheard having already observed (T., 1909, **95**, 495) that compounds of the type $CS<^{NR}_{NR}>CH_2$ (where R is an aryl radicle, not substituted in the para-position) are especially sensitive to hydrolysis.

Benzaldehyde, salicylaldehyde, and cinnamaldehyde show evidence of condensation with thiocarbamide; from certain ketones, too, the 'hydrochlorides' of basic substances are very slowly producible. On these subjects, as well as on the mechanism of the carbamide–aldehyde condensation—an example of which is mentioned below—it is proposed to make further inquiry.

Experimental.

Acetaldehyde and Thiocarbamide.

From a cold aqueous solution of thiocarbamide, mixed with acetaldehyde and acidified with nitric, hydrochloric, or sulphuric acid, a white solid was soon precipitated. Boiling water extracted from the latter a material, separating, as the solution cooled, in brilliant, vitreous prisms; this, the secondary condensation product, will be referred to subsequently.

The residue, a white, microcrystalline powder, was the condensation product, $CSN_2H_2{\cdot}CHMe$.

Found: N = 27·6; S = 31·7.

$C_3H_6N_2S$ requires N = 27·45; S = 31·37 per cent.

At about 212° (uncorr.) it melted, with copious effervescence, to a deep brown liquid, the decomposition temperature depending somewhat on the rate of the preliminary heating. Almost insoluble in water or in most of the common organic solvents, the compound dissolved gradually in hot dilute mineral acids, being hydrolysed into acetaldehyde and thiocarbamide. By hot alkali hydroxide it was readily decomposed, the solution turning brown and emitting the peculiar acrylic odour noticeable when acetaldehyde is heated in the presence of an alkali.

Like results were obtained with phosphoric, tartaric, benzoic, boric, and acetic acids, the two last-named acting more slowly than the others. Tartaric acid gave the primary condensation product almost free from the soluble compound; on the other hand, with acetone as solvent (and hydrochloric acid), the product consisted almost entirely of the latter.

Paracetaldehyde behaved similarly, except that the process of condensation was less rapid.

The acidified mixture, kept to incipient turbidity, gave no precipitate with alkali or with picric acid, and hence contained but

little of the base, $NH_2 \cdot C(:NH) \cdot S \cdot CHMe \cdot OH$. Some, however, was present, for the mixture, when treated in the cold with an alkaline solution of a lead salt, gave a yellowish-brown precipitate, quickly becoming black (in these circumstances thiocarbamide alone is but slowly desulphurised, whilst the condensation product is not affected).

The soluble product, referred to above, when recrystallised from alcohol, formed silvery, flattened prisms, decomposing with browning and effervescence at about 209° (uncorr.). Desulphurisation occurred readily on warming with an alkaline solution of a lead salt, the penetrating odour of 'aldehyde' being evolved.

Found: N = 19·2; S = 22·3.

$C_5H_{10}ON_2S$ requires N = 19·15; S = 21·92 per cent.

Differing from the primary condensation product by C_2H_4O, the above was plainly an additive compound of the latter. It does not seem to be producible by direct union; a sample of the insoluble material (previously boiled out with water and dried), after long keeping with acetaldehyde, slightly acidified, when collected and boiled with water yielded to this no crystalline substance.

Neither of the foregoing products was acetylated by boiling with acetyl chloride or with acetic anhydride.

Reference has been made above to a base,

$$NH_2 \cdot C(:NH) \cdot S \cdot CHMe \cdot OH.$$

Its 'hydrochloride,' quite stable in the absence of water, was obtained by mixing α-chloroethyl alcohol with a trifle less than one molecular proportion of thiocarbamide, and exposing the resultant clear syrup for several days in a vacuum over dishes containing respectively lime and sulphuric acid. Presently it became hard and odourless.

Found: HCl = 22·6.

$C_3H_8ON_2S,HCl$ requires HCl = 23·32 per cent.

The same 'hydrochloride,' or additive compound, was obtained by adding one molecular proportion of acetaldehyde to solid thiocarbamide hydrochloride (on a balance, because, at first, the aldehyde distilled off rather freely). (Found, HCl = 23·2. Calc., HCl = 23·32 per cent.)

In aqueous solution the product gave with picric acid a curdy, orange-yellow precipitate, easily hydrolysed; with sodium carbonate, a white, amorphous solid, at first soluble in acid, but presently becoming insoluble. After a time (varying with the concentration), the plain, aqueous solution also became turbid, the precipitate being insoluble in acid; in both cases the insoluble material was the non-basic compound, $CSN_2H_2{:}CHMe$.

When gaseous acetaldehyde was led into a suspension of thio-

carbamide in ether containing nitric acid, the thiocarbamide liquefied almost completely to a pasty, white syrup, decomposed by water into free nitric acid and a solid, the latter consisting largely of ethylidenethiocarbamide, $CSN_2H_2{:}CHMe$; from these properties the syrup (not analysed) was evidently the 'nitrate,' corresponding with the 'hydrochloride.'

Ethoxyethyl Iminothiocarbamate, $NH_2{\cdot}C(:NH){\cdot}S{\cdot}CHMe{\cdot}OEt$.

When hydrogen chloride was passed into a mixture of acetaldehyde and alcohol containing thiocarbamide in suspension, a liquid separated, clear at first, but presently becoming turbid. The white syrup, exposed as before in a vacuum, gave on analysis:

Found: $HCl = 21{\cdot}4$.

$C_5H_{12}ON_2S,HCl$ requires $HCl = 19{\cdot}8$ per cent.

Hence, the desired reaction:

$$CS(NH_2)_2 + CHMeCl{\cdot}OEt \longrightarrow \begin{matrix} NH_2 \\ NH_2 \end{matrix}\!\!>\!C{:}S\!<\!\begin{matrix} CHMe{\cdot}OEt \\ Cl \end{matrix},$$

had not occurred sharply, and, in effect, the product failed to yield a clear solution in water, some of the ordinary condensation product separating. By filtration, however, a clear solution was obtained, which yielded a sparingly soluble picrate and, on neutralisation with sodium hydrogen carbonate, a white, amorphous base:

Found: $S = 21{\cdot}54$.

$C_5H_{12}ON_2S$ requires $S = 21{\cdot}62$ per cent.

An almost pure salt was obtained by treating thiocarbamide hydrochloride with an alcoholic solution of acetaldehyde; the transparent, viscid syrup gave with water a clear solution, not becoming turbid on keeping, and having all the properties of the clarified solution obtained from the foregoing impure salt.

Found: $HCl = 19{\cdot}9$. Calc., $HCl = 19{\cdot}8$ per cent.

Compared with the hydroxy-base, this ethoxy-derivative was highly stable, but in a week or so it began to change, failing to dissolve completely in dilute acids:

$$NH_2{\cdot}C(:NH){\cdot}S{\cdot}CHMe{\cdot}OEt \longrightarrow EtOH + CSN_2H_2{:}CHMe.$$

When hydrogen chloride was passed into a suspension of thiocarbamide in excess of acetaldehyde, the product contained $HCl = 18{\cdot}7$, against 18·2 per cent., calculated for $CSN_2H_4,2CHMeO,HCl$, and hence, no doubt, was the 'hydrochloride' of the base which yields the secondary condensation product. Thiocarbamide hydrochloride, with excess of acetaldehyde, gave a similar result, except that the combined hydrogen chloride was about 2 per cent. higher

than before; in both cases some of the primary 'hydrochloride' was present.

Although very weak acids may bring about the condensation, it does not seem to occur in the total absence of free acid. Thus, when freshly prepared acetaldehyde was mixed with a solution of thiocarbamide in water previously boiled and allowed to cool, several days passed before a turbidity began to show; the mixture was now perceptibly acid, and on filtration (which increased the acidity) quickly became turbid again. The solution was neutralised exactly by ammonia, filtered, corked up, and set aside. For two days it remained clear, then turbidity recommenced, and, on testing, the liquid was found to be acid once more. Finally, the mixture, cleared and neutralised, was exposed freely to the air; it now rapidly became acid, and concurrently developed a voluminous, white precipitate.

Formaldehyde and Thiocarbamide.

Of the phenomena observed with these components, a brief account will suffice, the results being essentially similar to those set forth above. Instead of formaldehyde, the 40 per cent. aqueous solution, "formalin," was used.

In moderately dilute aqueous mixtures, acidified and containing but a slight excess of the aldehyde, precipitation was rapid, the white, sub-crystalline residue, left after extraction with boiling water, having the composition $CSN_2H_2{:}CH_2$.

Found: S = 36·1.

$C_2H_4N_2S$ requires S = 36·36 per cent.

Excess of formaldehyde hinders the precipitation, and, if great, may stop it altogether, especially if the solutions are highly concentrated.

The powder, almost insoluble in all the common solvents, melted (that is, decomposed), with browning and effervescence, at about 202—203° (uncorr.). Hot dilute mineral acids—but not vegetable acids—hydrolysed the substance into thiocarbamide and formaldehyde; the presence of the latter, in this and in other cases mentioned below, was recognised by Rimini's method (*Amer. Chem. J.*, 1900, **22**, 132). Desulphurisation occurred readily on warming with an alkaline solution of a lead salt. From thiocarbamide and α-chloromethyl alcohol, Hemmelmayr (*Monatsh.*, 1891, **12**, 90) has obtained a compound, $C_2H_4N_2S$, behaving with mineral and with vegetable acids in the way just mentioned, and melting at about 200°. From the materials named, one might have anticipated the formation of the salt of an *iso*thiocarbamide base. No doubt, such

a compound was formed and then decomposed, as shown by the scheme:

$$CS\langle^{NH_2}_{NH_2} + Cl\cdot CH_2\cdot OH \rightarrow {}^{NH_2}_{NH_2}\rangle C{:}S\langle^{CH_2\cdot OH}_{Cl} \rightarrow$$

$${}^{NH_2}_{NH}\rangle C\cdot S\cdot CH_2\cdot OH \rightarrow CS\langle^{NH_2}_{NH\cdot CH_2\cdot OH} \rightarrow CS\langle^{NH}_{NH}\rangle CH_2.$$

Hydrogen chloride, when led into a paste of thiocarbamide and formalin in molecular proportions, produced a clear syrup, CSN_2H_4,CH_2O,HCl.

Found: $HCl = 25{\cdot}2$.

$C_2H_6ON_2S,HCl$ requires $HCl = 25{\cdot}6$ per cent.

In every way the aqueous solution behaved like that of the higher homologue; the base precipitated from it on neutralisation changed, however, very rapidly into the condensation product, $CSN_2H_2{:}CH_2$.

By the following method, not entailing the use of an 'external' catalyst, the picrate of the base was isolated. To thiocarbamide, dissolved in a saturated aqueous solution of picric acid, a slight excess of formaldehyde was added. After a few minutes, well-formed, orange-yellow, slender prisms began to separate, which were soon removed, washed with ether, and dried (if the mixture is kept, it presently becomes grumous, the picrate being partly hydrolysed, with separation of the insoluble condensation product).

Found: $S = 9{\cdot}5$.

$C_2H_6ON_2S,C_6H_3O_7N_3$ requires $S = 9{\cdot}55$ per cent.

When heated, the picrate turned deep orange-red, then flared, evolving yellow fumes and leaving a voluminous, black residue.

With thiocarbamide and excess of formaldehyde, hydrogen chloride gave a syrup, yielding with water a very acid solution [the primary 'hydrochloride' (see above) is rapidly decomposed by water]; this solution, when neutralised with sodium hydrogen carbonate, gave a white powder decomposed by hot alkali with the formation of thiocarbamide and formaldehyde.

Found: $S = 27{\cdot}5$.

$C_3H_6ON_2S$ requires $S = 27{\cdot}12$ per cent.

Therefore, the syrup was the secondary 'hydrochloride.'

Formaldehyde and Carbamide.

Hemmelmayr (*loc. cit.*), from α-chloromethyl alcohol and carbamide, obtained a compound, $CON_2H_2{:}CH_2$. By acidifying a mixture of carbamide and formalin in water, the same compound was produced in a few seconds, the yield being 95 per cent. of the theoretical. (Found, $N = 38{\cdot}4$. Calc., $N = 38{\cdot}89$ per cent.)

No change was visible at 230° (Hemmelmayr does not record the melting point). There is reason to believe that a base exists precedently to the condensation product; but this is a matter lying outside the scope of the present paper, which is concerned with thiocarbamides only.

Methylene Di-iodide and Thiocarbamide.

Union occurred readily in presence of hot alcohol, two molecules of thiocarbamide being required to absorb one molecule of the di-iodide; the product, a crystalline, neutral salt, not freely soluble in alcohol or in water, when recrystallised from hot water formed very brilliant, colourless plates. From the aqueous solution, by treatment with a slight deficiency of *N*/10-alkali, the base was obtained as a voluminous, white precipitate, melting, with preliminary softening, at 198° (uncorr.).

Found: S = 38·5.

$C_3H_8N_4S_2$ requires S = 39·0 per cent.

With excess of silver nitrate, the salt yielded a precipitate of silver iodide; the residual solution was not blackened by ammonia, but, instead, gave a bright yellow precipitate. Hence, the non-acidic fraction is an *iso*thiocarbamide base,

$NH_2{\cdot}C(:NH){\cdot}S{\cdot}CH_2{\cdot}S{\cdot}C(:NH){\cdot}NH_2$.

Substituted Thiocarbamides and Aldehydes.

Allylthiocarbamide and Formaldehyde.—The liquid obtained by gently warming the constituents with concentrated hydrochloric acid, changed in a vacuum to a clear, viscid jelly, soluble in water, having the formula $CSN_2H_3(C_3H_5),CH_2,HCl$.

Found: HCl = 19·6.

$C_5H_{10}ON_2S,HCl$ requires HCl = 20·0 per cent.

The aqueous solution gave a picrate, and on neutralisation with sodium carbonate a clear oil, slowly changing, in a vacuum, to a brittle solid, $CSN_2H(C_3H_5){:}CH_2$.

Found: N = 21·35; S = 24·6.

$C_5H_8N_2S$ requires N = 21·8; S = 25·1 per cent.

Allylthiocarbamide and Acetaldehyde.—With concentrated hydrochloric acid, or with hydrogen chloride, the product was a syrup, $CSN_2H_3(C_3H_5),C_2H_4O,HCl$, becoming hard in a vacuum.

Found: HCl = 18·02.

$C_6H_{12}ON_2S,HCl$ requires HCl = 18·57 per cent.

Neutralisation of the aqueous solution yielded either an oil, slowly hardening, or (by the use of dilute solution and dilute

alkali) a granular, easily fusible solid; both substances gave nearly the same analytical figures. In three different preparations:

Found: N = 18·5, 18·4; S = 20·45, 19·7, 20·45.
$C_6H_{12}ON_2S$ requires N = 17·5; S = 20·0 per cent.

Although the mean figure for S is but 0·2 per cent. above the calculated value, that for N is nearly 1 per cent. too high. Nevertheless, the substance consisted mainly, if not entirely, of the free base, $C_3H_5{\cdot}NH{\cdot}C(:NH){\cdot}S{\cdot}CHMe{\cdot}OH$. It was sparingly soluble in cold, but quite appreciably so in hot, water; readily soluble in dilute acetic acid; both solutions gave a bright yellow picrate, soon becoming viscid, even in the cold. From the solution in an acid, the base was precipitated on the addition of an alkali, and dissolved again on treatment with an acid; no evidence was obtained of a condensation product.

Phenylthiocarbamide and Formaldehyde.—Gaseous hydrogen chloride was used, the resultant syrup hardening imperfectly in a vacuum.

Found: HCl = 17·1.
$C_8H_{10}ON_2S$,HCl requires HCl = 16·7 per cent.

The solution in dilute alcohol gave a picrate; with alkali hydroxide a white precipitate was obtained, partly soluble in acid, the resultant solution also yielding a picrate, but soon becoming turbid if allowed to remain. Sodium carbonate, when added to the solution in weak alcohol, gave a pasty precipitate, which changed presently to a brittle solid, melting at 159—160° (uncorr.), having the formula $CSN_2H(C_6H_5){:}CH_2$.

Found: S = 18·5.
$C_8H_8N_2S$ requires S = 19·5 per cent.

When heated with dilute alkali hydroxide, the compound was hydrolysed into phenylthiocarbamide and formaldehyde.

In another experiment, where the concentrated aqueous acid was used, and two molecular proportions of formaldehyde, the precipitate obtained with sodium carbonate melted, rather indefinitely, at about 105°, and had the formula $CSN_2H(C_6H_5){:}CH_2,CH_2O$.

Found: N = 14·3; S = 16·1.
$C_9H_{10}ON_2S$ requires N = 14·4; S = 16·48 per cent.

Phenylthiocarbamide and Acetaldehyde.—Paracetaldehyde, giving a cleaner product than acetaldehyde, was substituted for the latter. When warmed with concentrated hydrochloric acid, the mixture became liquid, and after about ten minutes a white oil began to separate, which presently became stiff; this—no doubt the 'hydrochloride'—was not analysed. Its alcoholic solution

yielded with sodium carbonate, first a yellow dough, which was rejected, and then a finely divided, white solid,

$$CSN_2H(C_6H_5):CH\cdot CH_3;$$

when boiled with alcohol (to remove any phenylthiocarbamide), this melted at 166—167° (uncorr.):

Found: N = 15·4; S = 18·06.

$C_9H_{10}N_2S$ requires N = 15·74; S = 17·97 per cent.

By boiling with an alkaline solution of a lead salt, the compound was desulphurised, with the evolution of acetaldehyde.

ab-*Diphenylthiocarbamide and Formaldehyde.*—Gaseous hydrogen chloride yielded a clear, pale yellow, tenacious oil,

$$CSN_2H_2(C_6H_5)_2,CH_2O,HCl.$$

Found: HCl = 12·4.

$C_{14}H_{14}ON_2S,HCl$ requires HCl = 12·39 per cent.

On contact with water, it changed mostly to a white, insoluble solid which, on crystallisation from alcohol, gave thiocarbanilide (m. p. 151°); in the water there was a very perceptible amount of dissolved base, which gradually decomposed, yielding thiocarbanilide.

The hydrochloride, freely miscible with alcohol, yielded with it a clear acid solution which, after neutralisation with sodium hydrogen carbonate, was poured into water. A white oil separated, changing gradually to a somewhat pasty solid, which was several times recrystallised from alcohol. Although, in the cold, the granular deposit was not very freely soluble, it was always viscid, and when the process had been thrice repeated, crystalline matter began to separate along with the former. Each product, when heated with dilute hydrochloric acid, gave the reaction of formaldehyde, and therefore probably contained methylenethiocarbanilide; but the material was obviously decomposing.

A repetition of the experment, absolute alcohol being used instead of 93 per cent. alcohol, led to a worse result, the solid this time being mixed with a visible amount of some oily material.

A pure specimen of the compound, $CS\langle^{NPh}_{NPh}\rangle CH_2$, being not yet to hand, methyleneaniline was heated with phenylthiocarbimide at 180°, and the resultant red oil shaken with light petroleum (to remove unchanged thiocarbimide); the remainder was then dissolved in alcohol. On keeping, a little solid matter separated, containing not a trace of methylenethiocarbanilide. The liquid portion gave the reaction of formaldehyde, but as methyleneaniline is readily hydrolysed, the fact affords no evidence that methylenethiocarbanilide had been produced.

ab-*Diphenylthiocarbamide and Acetaldehyde.*—With gaseous

hydrogen chloride, liquefaction was not quite complete, the syrup having a pasty appearance.

Found: HCl = 12·9.

$C_{15}H_{16}ON_2S,HCl$ requires HCl = 11·83 per cent.

Acetaldehyde was produced on heating with alkali hydroxide, and water extracted same basic material. No condensation product could be isolated; the alcoholic solution, when neutralised, gave a white solid, but this, on crystallisation from alcohol, was obtained as thiocarbanilide.

From the results of this and of the preceding experiment it appears that, although an increase in the number of the substituent radicles does not affect the power of the thiocarbamide to form a salt, it has a marked effect (at least where two aryl radicles are present) in diminishing the stability of the corresponding base, or of whatever condensation product it may tend to furnish. In the case of formaldehyde–thiocarbanilide, it is probably the condensation product that is particularly unstable; for the solid obtained by neutralisation of the 'hydrochloride' fails to dissolve in dilute acids, whereas (as already stated) water extracts from the latter a quite recognisable amount of material, behaving as the salt of a base.

ab-*Diphenyl*-a-*methylthiocarbamide and Acetaldehyde.*—Gaseous hydrogen chloride was used, the product, CSN_2HMePh_2,C_2H_4O,HCl, being a clear oil.

Found: HCl = 11·96.

$C_{16}H_{18}ON_2S,HCl$ requires HCl = 11·40 per cent.

On heating with alkaline lead solution, decomposition occurred readily, with blackening and the evolution of acetaldehyde. When treated with water, the 'hydrochloride' mostly dissolved (the original thiocarbamide is insoluble in water), the clear solution giving a bright yellow picrate, which soon became viscid. From the above clear solution, on neutralisation, an oil was deposited, presently becoming hard; the resultant solid, when recrystallised from alcohol, gave pure *ab*-diphenylmethylthiocarbamide.

Formaldehyde was used with precisely similar results. As with a trisubstituted thiocarbamide condensation cannot occur, one might perhaps have anticipated the formation, from the 'hydrochloride,' either of a base, $R_2N{\cdot}C(:NR){\cdot}S{\cdot}CHR{\cdot}OH$, or of its transposition product, $R_2N{\cdot}CS{\cdot}NR{\cdot}CHR{\cdot}OH$. The base, evidently, is susceptible of existence, but whether it decomposes directly into $MePhN{\cdot}C(:NPh){\cdot}SH \longrightarrow MePhN{\cdot}CS{\cdot}NHPh$, or whether migration of the oxidised radicle first occurs, with production of an unstable thiocarbamide, $MePhN{\cdot}CS{\cdot}NPh{\cdot}CHR{\cdot}OH$, was not investigated.

ab-*Diphenyl*-ab-*dimethylthiocarbamide and Acetaldehyde.*—In the presence of hydrogen chloride, union occurred precisely as in all the foregoing cases, and just as readily, a clear liquid being formed, which became viscid on keeping in a vacuum.

Found: HCl = 11·05.

$C_{17}H_{20}ON_2S,HCl$ requires HCl = 11·04 per cent.

By heating with dilute alkali hydroxide and a salt of lead—a treatment which has no effect on the parent thiocarbamide—the additive compound was very readily decomposed into methylaniline, acetaldehyde, chloride, carbonate, and sulphide. The tendency of thiocarbamidic sulphur, when engaged with a purely hydrocarbon radicle, to separate from the resultant molecule in combination with that radicle is well known; in the present case, the withdrawal of the sulphur is accomplished by a radicle, not purely hydrocarbon. Why the group CHMe(OH)· should hold to the sulphur in one case, and in others should wander away from it, like an acyl radicle, may depend on how far that group is electropositive, or electronegative, as compared with the rest of the molecule.

Acylated Condensation Products.

Earlier, it has been mentioned (p. 1251) that ready-formed $CS<^{NH}_{NH}>CHMe$ is not acetylated by boiling with acetic anhydride; attempts, therefore, were made to condense acyl substituted thiocarbamides with acetaldehyde.

Primary union occurred as usual, syrups being formed which became hard in a vacuum, and in the aqueous solution of each 'hydrochloride' a base was detectable by the methods already given; consequently, the presence of an acyl group in the thiocarbamide does not prevent the radicle, ·CHMe·OH, from uniting with the sulphur atom. Nevertheless, in no case was an acyl condensation product isolated, the bases changing very readily through hydrolysis. Gaseous hydrogen chloride was employed.

The 'hydrochloride' from acetylthiocarbamide was contaminated with the non-acylated compound, CSN_2H_4,C_2H_4O,HCl, and from the mixture the condensation product corresponding with the latter alone was separated in a pure condition.

That from benzoylthiocarbamide was obtained almost pure (Found, HCl = 14·12. $CSN_2H_3(COPh),MeCHO,HCl$ requires HCl = 14·06 per cent.); it formed a brittle, deliquescent resin; the base precipitated from which soon decomposed, yielding benzoylthiocarbamide.

Carbethoxythiocarbamide gave a transparent 'hydrochloride' (Found, HCl = 15·2; $CSN_2H_3·CO_2Et,C_2H_4O,HCl$ requires HCl =

15·97 per cent.). Its alcoholic solution, when treated with water, yielded an oily base; but the oil soon hardened, changing into carbethoxythiocarbamide.

Hitherto, the migration of groups from sulphur to nitrogen, with consequent change of an *iso*thiocarbamide to a normal thiocarbamide, has been observed only when that group is distinctly electronegative. Where a base, AcNH·C(NH)·S·CHR·OH, is concerned, it may well be that the group ·CHR·OH, at best but feebly acidic, cannot migrate to form a diacylthiocarbamide. Diacylthiocarbamides, too, are difficult of production, and the few known examples are all very unstable, being easily hydrolysed back again into monoacylthiocarbamides, and, in presence of mineral acids, possibly (see below) even into thiocarbamide itself. Despairing, after numerous experiments, in which the conditions were varied in many ways, of securing direct condensation, we tried an indirect method, and this time successfully.

Carbethoxythiocarbimide and Aldehyde–Ammonia.—In the presence of acetone the components united vigorously, the product, recrystallised a few times from alcohol, occurring in small, colourless prisms melting at 152—153° (uncorr.). Desulphurisation took place readily on heating with an alkaline solution of a lead salt, or with ammoniacal silver nitrate, acetaldehyde being produced.

Found: N = 16·7; S = 18·6.

$C_6H_{10}O_2N_2S$ requires N = 16·09; S = 18·39 per cent.

Equal molecules therefore unite, the resultant compound, EtO·CO·NH·CS·NH·CHMe·OH, by loss of H_2O, yielding either

$$CS\begin{<}\begin{matrix}N(CO_2Et)\\NH\text{——}\end{matrix}\end{>}CHMe \quad \text{or} \quad CS\begin{<}\begin{matrix}NH\cdot CO_2Et\\N{:}CHMe\end{matrix}\end{>}.$$

Nearly insoluble in water, the compound dissolved gradually in hot dilute acids, acetaldehyde being expelled; on cooling, the solution deposited brilliant crystals melting at 138—139° and consisting of carbethoxythiocarbamide. The identity was confirmed by the mixed melting-point method.

By treatment with concentrated alkali hydroxide, thiocyanic acid was abundantly produced; under like conditions, carbethoxythiocarbamide gave not a trace. Therefore, in the hydrolysis an *aa*-disubstituted thiocarbamide is formed (Hugershoff, *Ber.*, 1899, **32**, 3649; compare also Wheeler, *Amer. Chem. J.*, 1902, **27**, 270; Dixon and Hawthorne, T., 1907, **91**, 131; Dixon and Taylor, *ibid.*, 1908, **93**, 27). According to the first formula, given above, the addition of water may furnish hydrogen to either, or both, of the nitrogen atoms, and if any of it goes to the group ·NH· an *aa*-disubstituted thiocarbamide must result, namely,

$$NH_2\cdot CS\cdot N(CO_2Et)\cdot CHMe\cdot OH.$$

This would give $H\cdot NCS \longrightarrow H\cdot SCN$ and

$$CO_2Et\cdot NH\cdot CHMe\cdot OH \longrightarrow CHMeO + NH_2\cdot CO_2Et.$$

On the other hand, the compound $CO_2Et\cdot NH\cdot CS\cdot N{:}CHMe$ could not yield, either through hydrolysis or by any reasonably presumable kind of transposition, an *aa*-disubstituted thiocarbamide.

Carbomethoxythiocarbimide and Aldehyde–Ammonia.—Prepared as in the last case, colourless prisms were obtained melting at 187·5° (corr.).

Similarly, by boiling with dilute acid, the product was hydrolysed, the solution, as it cooled, depositing brilliant crystals of carbomethoxythiocarbamide (m. p. 165—166°).

With concentrated alkali hydroxide, the substance behaved in the same way as the foregoing homologue; carbomethoxythiocarbamide, when subjected to the same treatment, gave no reaction for thiocyanic acid. To the above carbomethoxy-condensation product, therefore, we assign the structure $CS\langle^{N(CO_2Me)}_{NH}\!\!>\!CHMe$.

In respect of chemical properties generally, it behaved exactly like the homologue.

Found: N = 17·5; S = 20·5.

$C_5H_8O_2N_2S$ requires N = 17·5; S = 20·0 per cent.

Acetylthiocarbimide and Aldehyde–Ammonia.—Vigorous union occurred in presence of acetone; no external cooling was used, and after a few recrystallisations from alcohol, minute, white needles were obtained melting at 197—198° (uncorr.).

Found: C = 41·5; H = 6·6; N = 19·4; S = 22·3.

$C_5H_8ON_2S$ requires C = 41·7; H = 5·6; N = 19·4; S = 22·2 per cent.

Consequently, the reaction had run the course:

$$COMe\cdot NCS + CHMe(OH)\cdot NH_2 \longrightarrow C_5H_8ON_2S + H_2O;$$

but it is far from quantitative, and in one of the experiments the only substance definitely isolated was acetylthiocarbamide.*

In the main, the compound resembled the two carboalkyloxy-derivatives above mentioned; but although it was readily hydrolysed by hot dilute mineral acids, the resultant solution did not yield acetylthiocarbamide. By direct experiment it was found that the latter is itself very easily hydrolysed into thiocarbamide and acetic acid. With concentrated alkali hydroxide it yielded no thiocyanic acid; this, however, is not surprising, acetylthiocarbamide being decomposed very rapidly, even in the cold, by a solution of alkali containing less than 0·2 per cent. of hydroxyl. A concentrated solution of alkali is required to effect the "thio-

* At about 0°, the same constituents yield also a compound, $C_7H_{15}O_2N_3S$ (Dixon, T., 1892, **61**, 530); it is composed of

$$MeCO\cdot NCS + 2MeCHO, NH_3 - H_2O.$$

cyanic" decomposition of *aa*-disubstituted thiocarbamides; in the case of a compound such as $NH_2 \cdot CS \cdot N(COMe) \cdot CHMe \cdot OH$, the acetyl group is probably withdrawn so rapidly that an *aa*-configuration is destroyed as fast as it is formed. Quite possibly, the acetyl is eliminated before the hydrolytic opening of the ring even commences.

Having regard to these considerations, and to the general analogies in respect to properties, method of formation, and the essential hydrolytic change by acids, with production of acetaldehyde, we are disposed to attribute to the compound a structure like that of its congeners, that is, $CS\langle^{N(COMe)}_{NH}\rangle CHMe$.

Hydrocarbon thiocarbimides give with aldehyde–ammonia (Dixon, T., 1888, **53**, 411; 1892, **61**, 509) basic compounds, possibly of the form $CS\langle^{NR \cdot CHMe}_{NR \cdot CHMe}\rangle NH$. In various ways it was attempted, by adding one molecule of water, to break off $NH_3 + MeCHO$, and thus to obtain the condensation products, $CS\langle^{NR}_{NH}\rangle CHMe$. All the attempts were fruitless, the disruption, once started, leading to the simultaneous expulsion of both the ethylidene groups, with the formation of a mono-substituted thiocarbamide.

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[*Received, November 5th*, 1916.]

XC.—*The Dual Theory of Acid Catalysis. A Comparison of the Activities of Certain Strong Acids.*

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ACCORDING to what has been termed the dual theory of the catalytic action of acids, the observed catalytic effect is the sum of two separate effects in which the active agents are supposed to be the hydrogen ion and the non-ionised acid respectively. In a certain sense, such catalysed reactions are of composite character in that two simultaneous and independent changes occur, for which the initial and final products are identical. The essential difference between these two reactions lies in the fact that the two catalysts

are in general of unequal catalysing power. If the reaction takes place with uniform velocity v, then v is given by the equations

$$v = v_{\mathrm{H}} + v_{\mathrm{M}} = k_{\mathrm{H}} c\alpha + k_{\mathrm{M}} c(1 - \alpha),$$

in which v_{H} and v_{M} are the velocities of the simultaneous reactions, k_{H} and k_{M} the activity-coefficients of the hydrogen ion and the non-ionised acid respectively, c is the concentration of the acid, and α its degree of ionisation.

The validity of this equation has already been shown to receive support from the results of experiments on the rate of isomeric change of acetone under the influence of hydrochloric, dichloroacetic, $\alpha\beta$-dibromopropionic, monochloroacetic, and acetic acids as catalysts (Dawson and Powis, T., 1913, **103**, 2135), and by observations on the catalytic effect produced by monochloroacetic acid in the presence of varying quantities of the corresponding salts (Dawson and Reiman, T., 1915, **107**, 1426). All the above acids gave very nearly the same value for k_{H}, whereas k_{M} was found to diminish rapidly as the tendency of the acid to ionise decreases. This relation had already been pointed out by Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 211) from the results of his own and previous observations on the kinetics of acid catalysed reactions, mainly in methyl- and ethyl-alcoholic solution. According to Taylor (*Meddel. K. Vetensk. Nobelinst.*, 1914, **3**, No. 1), the connexion between the activity of the (non-ionised) acid and the tendency of the acid to ionise is approximately given by the equation $k_{\mathrm{M}}/k_{\mathrm{H}} = \sqrt{K}$, in which K is the ionisation-constant of the acid.

It is well known that the strongest acids do not conform at all to the requirements of the dilution law in solutions of moderate concentration, and the relative catalytic activities of these acids cannot therefore be estimated even approximately on the basis of the above relation. The behaviour of hydrochloric acid would seem to show, however, that the catalysing power of these strong acids in the non-ionised condition is greater than that of the ionised acids. For this reason the investigation of the strong acids is of special interest, and in this paper experiments are described in which the authors have made a comparison of the catalytic effects produced by hydrobromic, trichloroacetic, trichlorobutyric, and *p*-toluenesulphonic acids. All these acids may be said to belong to the group of strong acids, and they all diverge widely from the requirements of the dilution law in that $(c\alpha)^2/c(1-\alpha)$ increases rapidly with increasing concentration over the range of concentrations at which the activity of the acids was examined.

The evaluation of k_{H} and k_{M} involves the determination of the velocity of the catalysed reaction for two values of c, and for each

concentration it is necessary to know the degree of ionisation of the acid.

The accuracy with which the ratio k_M/k_H for the strong acids can be determined is to some extent limited by the circumstance that the ionisation of the acids cannot be fixed with any great degree of precision. At present the only method which can be applied in the estimation of the degree of ionisation of the strong acids over the range 0·01 to 1·0 mol. per litre is the conductivity method. It is generally recognised that the simple conductivity ratio Λ/Λ_∞ does not give the true degree of ionisation for solutions of this order of concentration, but that a correction must be applied for the viscosity of the solution, so that $\alpha = \Lambda/\Lambda_\infty \cdot f(\eta)$, where η is the relative viscosity. The nature of this correction has been discussed by Green (T., 1908, **93**, 2049), Johnston (*J. Amer. Chem. Soc.*, 1909, **31**, 1010), and Kraus (*ibid.*, 1914, **36**, 35), and from the available data it would seem that the correction to be applied for the influence of viscosity varies according to the nature of the ions. In general, the ionisation would appear to lie between the values given by

$$\alpha = \Lambda/\Lambda_\infty \quad \text{and} \quad \alpha' = \Lambda\eta/\Lambda_\infty .$$

For three of the acids examined by us, the difference between the values of α and α' in 0·2*N*-solution amounts to about 8 per cent., and since no adequate grounds can be advanced for the choice of either of the limiting values or of any particular intermediate value for the degree of ionisation, we have calculated the coefficients k_H and k_M in duplicate, using in the one case the ionisation given by $\alpha = \Lambda/\Lambda_\infty$, and in the other that given by $\alpha' = \Lambda\eta/\Lambda_\infty$.

In connexion with the application of these equations to the strong acids, due regard must be paid to the assumptions which are involved. According to measurements of the transport ratio of the hydrogen ion in hydrochloric acid (Noyes and Sammet, *J. Amer. Chem. Soc.*, 1902, **24**, 944; 1903, **25**, 165) and nitric acid (Noyes and Kato, *ibid.*, 1908, **30**, 318), it would seem that this ratio varies to a considerable extent with the concentration even in dilute solution. Whether the results obtained by these authors are accepted or not, there is no doubt that the transport number of the hydrogen ions varies in moderately concentrated solutions, and since the use of either of the above equations involves the assumption that the relative mobilities of the positive and negative ions are independent of the concentration, it must be admitted that the values of both α and α' are not unimpeachable. The uncertainty in the degree of ionisation which arises from the variation of the transport ratio increases with the concentration, and for this and other reasons we have limited the comparison of

the catalytic activities of the acids to concentrations between 0·01 and 0·2*N*.

Conductivity and Viscosity Measurements.

In the measurement of the conductivity, two cells of capacity 3 and 30 were employed. An Ostwald viscometer with an outflow period of about four minutes was used in the determination of the viscosities. All observations were made at 25 ± 0·01°.

Independent series of measurements of the conductivity were made for the several acids. From the actual observations three sets of curves were obtained by plotting the molecular conductivity against (1) the cube root of the concentration; (2) the logarithm of the concentration; and (3) the cube root of the dilution. The conductivities at the required concentrations were read off from the three curves, and the mean values are recorded in table I. Within narrow limits, the relative viscosity of the solutions can be represented as a linear function of the concentration, and the values recorded under η have been obtained by the use of the interpolation formula $\eta = 1 + Ac$, in which A is a constant characteristic of the acid.

TABLE I.

Hydrobromic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·5	1·0
Λ	418·8	411·4	400·3	391·9	382·5	362·9	334·5
η	1·0003	1·0007	1·0016	1·0033	1·0066	1·0165	1·0327

$\eta = 1 + 0{\cdot}0327\ c.$

Trichloroacetic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·5
Λ	374·5	365·0	348·5	332·6	309·8	262·8
η	1·0038	1·0077	1·0192	1·0385	1·077	1·192

$\eta = 1 + 0{\cdot}385\ c.$

Trichlorobutyric Acid.

c	0·01	0·02	0·05	0·1	0·2
Λ	352·4	334·3	301·7	269·6	227·8
η	1·0043	1·0087	1·0217	1·0435	1·087

$\eta = 1 + 0{\cdot}435\ c.$

p-*Toluenesulphonic Acid.*

c	0·01	0·02	0·05	0·1	0·2
Λ	371·4	363·6	351·6	341·6	330·3
η	1·0043	1·0087	1·0217	1·0435	1·087

$\eta = 1 + 0{\cdot}435\ c.$

In reference to the data in the above table, it may be noted that the recorded viscosities of the hydrobromic acid solutions are in good agreement with the results obtained by Reyher (*Zeitsch. physikal. Chem.*, 1888, **2**, 744). A close agreement is also found when the conductivities for solutions of trichlorobutyric acid are compared with the values given by Kendall (*Meddel. K. Vetensk. Nobelinst.*, 1913, **2**, No. 38). On the other hand, Kendall's data for trichloroacetic acid are appreciably smaller than those given above. The conductivity curves are approximately parallel over the entire range (0·01 to 0·2*N*), and the average difference amounts to no less than about 4 per cent. Although there is reason to suppose that our values are rather high, it would seem that the discrepancy is mainly due to the presence of foreign substances in Kendall's acid, which was admittedly unpurified. For dilute solutions of *p*-toluenesulphonic acid, conductivity measurements have been made by Wegscheider and Lux (*Monatsh.*, 1908, **30**, 411). At the highest comparable concentration ($c=0{\cdot}05$) the numbers obtained are almost identical, but with falling concentration the conductivity curves diverge, and at $c=0{\cdot}01$ our result is about 0·8 per cent. greater than the number given by Wegscheider and Lux.

Limiting Conductivities.

The data which have been used in the computation of the conductivity of the completely ionised acids may be briefly indicated. For the most part, the limiting ionic conductances are taken from the tables compiled by Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, **34**, 454). According to these tables, $H^{\cdot}=350$, but, on the other hand, Kendall (T., 1912, **101**, 1275) seems to have made out a good case for a lower value, namely, $H^{\cdot}=347{\cdot}2$. We have adopted the intermediate value $H^{\cdot}=348{\cdot}2$, which agrees with the limiting conductivity of hydrochloric acid ($\Lambda_{\infty}=424{\cdot}0$; $Cl'=75{\cdot}8$) recorded by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781).

Hydrobromic Acid.—$Br'=78{\cdot}0$, whence $\Lambda_{\infty}=426{\cdot}2$.

Trichloroacetic Acid.—Kendall (*loc. cit.*) gives $\Lambda_{\infty}=111{\cdot}2$ for the potassium salt. Since $K'=74{\cdot}8$, $\Lambda_{\infty}=111{\cdot}2-74{\cdot}8+348{\cdot}2=384{\cdot}6$.

Trichlorobutyric Acid.—Kendall gives $\Lambda_{\infty}=79{\cdot}8$ for the sodium salt. Since $Na'=51{\cdot}2$, $\Lambda_{\infty}=79{\cdot}8-51{\cdot}2+348{\cdot}2=376{\cdot}8$.

p-Toluenesulphonic Acid.—According to Wegscheider and Lux (*loc. cit.*), the potassium salt gives $\Lambda_{\infty}=107{\cdot}6$ and the sodium salt $\Lambda_{\infty}=84{\cdot}5$. These numbers yield 33·1 as a mean value for the *p*-toluenesulphonate ion, whence $\Lambda_{\infty}=348{\cdot}2+33{\cdot}1=381{\cdot}3$.

The above numbers have been employed in the derivation of the degree of ionisation of the various acids.

Velocities of Reaction.

Before the experimental data * are presented we would direct attention to certain features connected with the use of the equation

$$v = k_H c\alpha + k_M c(1-\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The quantities c and α are not independently variable, and the relation between them may obviously be utilised to eliminate α from the general equation. If the ionisation varies with the concentration in accordance with the law of mass action, then

$$(c\alpha)^2/c(1-\alpha) = K \quad \text{or} \quad \alpha = f(c,K) \quad . \quad . \quad . \quad . \quad (2)$$

For strong electrolytes, the relation between α and c can be expressed by Storch's equation (*Zeitsch. physikal. Chem.*, 1896, **19**, 13),

$$(c\alpha)^n/c(1-\alpha) = K \quad \text{or} \quad \alpha = f(c,K,n) \quad . \quad . \quad . \quad . \quad (3)$$

in which n is a constant which varies, however, from 1·4 to 1·6, according to the nature of the electrolyte.

More recently, Kraus and Bray (*J. Amer. Chem. Soc.*, 1913, **35**, 1315; compare also MacDougall, *ibid.*, 1912, **34**, 855) have shown that the connexion between c and α may be expressed quite generally by means of the equation

$$(c\alpha)^2/c(1-\alpha) = K + D(c\alpha)^m \quad \text{or} \quad \alpha = f(c,K,D,m) \quad . \quad . \quad (4)$$

in which K, D, and m are characteristic of the electrolyte concerned.

The constants in the Kraus-Bray equation are not known for the acids examined by us, but apart from this, the equation is of such a complicated nature that it would not be profitable to attempt to make use of it in connexion with equation (1). By comparison the Storch equation is quite simple, and as a first approximation this may be regarded as expressing quite generally the connexion between c and α. If for the strong acids we make $n = 1{\cdot}4$ (compare Bancroft, *Zeitsch. physikal. Chem.*, 1899, **31**, 188) and for the weak acids $n = 2$, then the velocity of reaction v may be expressed in terms of the one variable c and the three constants k_H, k_M, and K.

Instead of eliminating α from the velocity equation, we may, however, substitute for $c(1-\alpha)$, in which case equation (1) may be written in the form

$$v = k_H c\alpha + k'_M (c\alpha)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $k'_M = k_M / K$.

* The experimental method has been described in a previous paper (Dawson and Powis, *loc. cit.*).

If $n=2$, this becomes

$$v = k_H ca + k'_M(ca)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is identical in form with the empirical equation given by Arrhenius ("Lehrbuch," 1900, p. 174) to express the relation between the velocity of reaction and the concentration of the hydrogen ions. According to the above method of deduction, this equation should represent the results obtained with weak acid catalysts, but not those obtained with strong acids. On the other hand, equation (5) should be applicable to the strong acids, the catalytic activity of which forms the subject of this paper. In the actual testing of the experimental data we have, however, preferred to make use of the original equation, substituting for the degree of ionisation the value given by $\alpha = \Lambda/\Lambda_\infty$ or $\alpha' = \Lambda\eta/\Lambda_\infty$ without making any assumption in regard to the connexion between c and α (or α').

If for two concentrations, c_1 and c_2, the degrees of ionisation are α_1 and α_2, and the corresponding velocities of reaction v_1 and v_2, then $V_1 = v_1/c_1$ and $V_2 = v_2/c_2$ represent what may be termed the equivalent velocities of reaction at concentrations c_1 and c_2.

From

$$V_1 = k_H\alpha_1 + k_M(1-\alpha_1)$$

and

$$V_2 = k_H\alpha_2 + k_M(1-\alpha_2),$$

we obtain

$$k_H = \frac{V_1(1-\alpha_2) - V_2(1-\alpha_1)}{\alpha_1 - \alpha_2} \quad . \quad . \quad . \quad . \quad (7a)$$

$$k_M = \frac{V_2\alpha_1 - V_1\alpha_2}{\alpha_1 - \alpha_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

The extent to which the calculated velocity-coefficients k_H and k_M are affected by errors in α and V may readily be ascertained by reference to the data for a typical pair of experiments. For this purpose we may take the first and last experiments with trichloroacetic acid as catalyst (table III), that is to say, $c_1 = 0{\cdot}01$, $\alpha_1 = 0{\cdot}974$, $V_1 = 469 \times 10^{-6}$, and $c_2 = 0{\cdot}2$, $\alpha_2 = 0{\cdot}806$, and $V_2 = 502 \times 10^{-6}$.

By substitution in the above equations, it is seen that k_H and k_M are affected to approximately the same extent by a given error in the determination of the degree of ionisation and that they are not appreciably altered by a small change in the difference between α_1 and α_2. On the other hand, the coefficients are much more sensitive to errors in the determination of the equivalent velocity of reaction, and this applies particularly to k_M. If we assume an error of 1 per cent. in the determination of V_1 and V_2, and sub-

stitute the above data for trichloroacetic acid in the equations (7*a*) and (7*b*), we obtain $k_H = 464 \pm 6$ and $k_M = 660 \pm 52$. These figures show clearly that the evaluation of k_M for the highly ionised acids is particularly susceptible to errors in the measurement of the velocity of reaction.

Considerations of this nature have led to the adoption of the following method for the derivation of the velocity-coefficients. For each acid five measurements of the velocity of reaction were made at the following concentrations: (1) 0·01; (2) 0·02; (3) 0·05; (4) 0·1; (5) 0·2*N*. The coefficient k_H was obtained by taking the mean of the three values afforded by the combination of (1) and (5), (2) and (4), and (2) and (5). By substitution in the equation

$$k_M = (V - k_H)/1 - \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

each of the five experiments gives a value of k_M. The five values are not, however, equally trustworthy, for $(1-\alpha)$ approximates to zero with falling concentration. It is readily seen that the relative "weights" which should be assigned to the separate k_M values in the deduction of the probable mean are approximately in the ratio of the values of $(1-\alpha)$, and this requirement has been partly complied with by weighting the several values of k_M as follows: $c = 0{\cdot}01$ (weight = 1), $c = 0{\cdot}02$ (2), $c = 0{\cdot}05$ (3), $c = 0{\cdot}1$ (4), $c = 0{\cdot}2$ (5).

In the following tables, in which our results are recorded, the concentration of the acid, c, is given in the first column, the degree of ionisation, α (or α'), in the second, the value of k_M according to equation (8) in the third, the calculated velocities v_H, v_M, and $v = v_H + v_M$ in the fourth, fifth, and sixth respectively, the observed velocity of reaction, $v_{obs.}$, in the seventh, and the equivalent velocity, $V = v_{obs.}/c$, in the last. At the head of each table are given the mean values of k_H and k_M, derived by the method explained above, which have been used in the calculation of v_H, v_M, and v. For hydrobromic and trichloroacetic acids the results are given in duplicate, the first series of calculations being based on the ionisation values given by $\alpha = \Lambda/\Lambda_\infty$, and the second on those given by $\alpha' = \Lambda\eta/\Lambda_\infty$. In the case of trichlorobutyric and *p*-toluenesulphonic acids we give only the calculations which are based on the ionisation values afforded by $\alpha = \Lambda/\Lambda_\infty$. For the former acid k_H is almost equal to k_M, and changes in the assumed degree of ionisation have consequently little influence on the calculated velocities of reaction. In the case of *p*-toluenesulphonic acid it is found that the value of α' increases with the concentration between $c = 0{\cdot}1$ and $c = 0{\cdot}2$. Since the occurrence of a minimum in the ionisation of the acid in this interval of concentration is extremely improbable, it would seem that the viscosity correction involved in the equation for α' is in this case too large. For this reason the

observed velocities are only compared with those calculated on the assumption that the degree of ionisation is given by $\alpha = \Lambda/\Lambda_\infty$.

Table II.

Hydrobromic Acid.

$\alpha = \Lambda/\Lambda_\infty$, $k_H = 457 \times 10^{-6}$, $k_M = 665 \times 10^{-6}$.

c.	α.	$k_M \cdot 10^6$.	$v_H \cdot 10^6$.	$v_M \cdot 10^6$.	$v \cdot 10^6$.	$v_{obs.} \cdot 10^6$.	$V \cdot 10^6$.
0·00996	0·983	624	4·47	0·11	4·58	4·58	459·8
0·01992	0·965	683	8·78	0·46	9·24	9·26	464·9
0·0498	0·939	669	21·37	2·02	23·4	23·4	469·9
0·0998	0·920	670	41·96	5·31	47·25	47·3	474·0
0·1996	0·897	663	81·82	13·68	95·5	95·4	478·0

$\alpha' = \Lambda\eta/\Lambda_\infty$, $k_H = 456 \times 10^{-6}$, $k_M = 691 \times 10^{-6}$.

0·00996	0·983	682	4·46	0·12	4·58	4·58	459·8
0·01992	0·996	718	8·77	0·47	9·24	9·26	464·9
0·0498	0·941	692	21·37	2·04	23·4	23·4	469·9
0·0998	0·923	690	42·01	5·31	47·3	47·3	474·0
0·1996	0·903	682	82·20	13·38	95·6	95·4	478·0

Table III.

*Trichloroacetic Acid.**

$\alpha = \Lambda/\Lambda_\infty$, $k_H = 461 \times 10^{-6}$, $k_M 636 \times 10^{-6}$.

c.	α.	$k_M \cdot 10^6$.	$v_H \cdot 10^6$.	$v_H \cdot 10^6$.	$v \cdot 1_{obs.}$	$v_{obs.} \cdot 10^6$.	$V \cdot 10^{-6}$.
0·01001	0·974	750	4·49	0·17	4·66	4·69	468·5
0·02002	0·949	637	8·76	0·65	9·41	9·41	470·0
0·05005	0·906	595	20·90	2·99	23·9	23·7	473·5
0·1001	0·865	591	39·92	8·59	48·5	47·9	478·5
0·2002	0·806	673	74·38	24·70	99·1	100·5	502·0

$\alpha' = \Lambda\eta/\Lambda_\infty$, $k_H = 460 \times 10^{-6}$, $k_M = 707 \times 10^6$.

0·01001	0·977	830	4·50	0·16	4·66	4·69	468·5
0·02002	0·956	689	8·86	0·62	9·42	9·41	470·0
0·05005	0·923	622	21·30	2·70	24·0	23·7	473·5
0·1001	0·898	641	41·35	7·16	48·5	47·9	478·5
0·2002	0·867	776	79·84	18·66	98·5	100·5	502·0

* It has already been pointed out that the values given by Kendall (*loc. cit.*) for the conductivity of trichloroacetic acid are about 4 per cent. smaller than ours. Since the two Λ_∞ values only differ by about 0·2 per cent., it follows that the two series of α values show a considerable, although approximately constant, difference. If Kendall's interpolated ionisation values ($\alpha = \Lambda/\Lambda_\infty$) are used for the calculation of the coefficients k_H and k_M in the manner described above, we obtain as mean values $k_H = 458 \times 10^{-6}$ and $k_M = 600 \times 10^{-6}$. The difference produced in the ratio k_M/k_H is obviously not very great.

TABLE IV.

Trichlorobutyric Acid.

$\alpha = \Lambda/\Lambda_\infty$, $k_H = 467 \times 10^{-6}$, $k_H = 482 \times 10^{-6}$.

c.	α.	$k_M \cdot 10^6$.	$v_H \cdot 10^6$.	$v_M \cdot 10^6$.	$v \cdot 10^6$.	$v_{obs.} \cdot 10^6$.	$V \cdot 10^6$.
0·01005	0·934	477	4·38	0·32	4·70	4·70	467·7
0·01985	0·888	480	8·23	1·07	9·30	9·30	468·5
0·0496	0·802	491	18·57	4·73	23·3	23·4	471·8
0·1002	0·715	477	33·46	13·77	47·2	47·1	470·0
0·2001	0·603	482	56·62	38·46	95·1	95·1	472·9

TABLE V.

p-Toluenesulphonic Acid.

$\alpha = \Lambda/\Lambda_\infty$, $k_H = 472 \times 10^{-6}$, $k_M = 593 \times 10^{-6}$.

c.	α.	$k_M \cdot 10^6$.	$v_H \cdot 10^6$.	$v_M \cdot 10^6$.	$v \cdot 10^6$.	$v_{obs.} \cdot 10^6$.	$V \cdot 10^6$.
0·00999	0·974	608	4·59	0·15	4·74	4·75	475·5
0·02006	0·954	572	9·03	0·55	9·58	9·56	476·6
0·04995	0·922	606	21·74	2·31	24·05	24·1	482·5
0·1003	0·896	593	42·42	6·18	48·6	48·6	484·6
0·1998	0·866	591	81·66	15·88	97·5	97·5	488·0

Some experiments were also made with nitric acid as catalyst, but the results indicate that the reaction does not proceed quite normally in presence of this acid, especially at the higher concentrations. The disturbing factor not only makes itself evident in modifying the course of the reaction in a particular experiment, but the equivalent velocities calculated from the initial rate of change exhibit irregular and rather wide variations which are in marked contrast with the regular variation found in the case of the other acids. According to the numbers under V in tables II to V, the equivalent velocity increases continuously with the concentration when hydrobromic, trichloroacetic, and *p*-toluenesulphonic acids are used as catalysts. The same relation holds for hydrochloric acid (T., 1913, **103**, 2139). In the case of trichlorobutyric acid, the equivalent velocity shows small, irregular variations, but these can be accounted for by the normal experimental error. The anomalies observed with nitric acid are in all probability due to the oxidising action of the acid on the hydriodic acid.

If the observed and calculated velocities in tables II to V are compared, it will be seen that the differences are in no case greater than can be accounted for by errors of experiment. The measurements furnish, therefore, additional evidence in support of the theory of the dual nature of acid catalysis.

A much more stringent test of the validity of the theory is of course furnished by a comparison of the several values of k_M in each series. Except in the case of trichlorobutyric acid, to which

reference will be made later, the values of k_M calculated according to equation (8), and recorded in the third column of the preceding tables, are only very approximately constant. Due consideration must, however, be given to the circumstance that the acids are for the most part highly ionised at all the concentrations investigated, and that the effect due to the non-ionised acid is consequently only a small fraction of the total effect. This is evident from an inspection of the partial velocities v_H and v_M, which are recorded in the fourth and fifth columns of the tables.

Neither by comparison of the observed and calculated velocities nor by comparing the several k_M values is it possible to draw any conclusion with reference to the choice of α or α' as a measure of the degree of ionisation. The general agreement is of the same order in the two cases.

To facilitate the comparison of the several coefficients which have been calculated from the above experiments, the values of k_H and k_M are brought together in table VI, in which the ratio k_M/k_H is also shown. The two sections of the table give the numbers derived from α or α' respectively. In addition to the four acids investigated in this paper, we give the numbers for hydrochloric acid, which have been calculated in exactly the same way from experiments at concentrations between $c=0{\cdot}01$ and $c=0{\cdot}2$.

TABLE VI.

Acid.	$\alpha=\Lambda/\Lambda_\infty$ · $k_H\cdot10^6$.	$k_M\cdot10^6$.	k_M/k_H.	$\alpha'=\Lambda\eta/\Lambda_\infty$ · $k_H\cdot10^6$.	$k_M\cdot10^6$.	k_M/k_H.
Hydrochloric	461	757	1·64	461	781	1·70
Hydrobromic	457	665	1·46	456	691	1·52
Trichloroacetic	461	636	1·38	460	701	1·52
p-Toluenesulphonic	472	593	1·25	—	—	—
Trichlorobutyric	467	482	1·03	467	485	1·04

From this table it is clear that the ratio k_M/k_H varies quite appreciably in the above series of strong acids. In all cases the acid is more active in the non-ionised than in the ionised condition. The substitution of α' for α makes some difference in the values of the ratio, but the sequence is not altered thereby.

It may be noted, further, that the values of k_H in both series are fairly concordant. If we use the mean value of k_H—463×10^{-6} for the α series and 461×10^{-6} for the α' series—in the calculation of the coefficients for the non-ionised acid according to the method described above, it is found that the individual values of k_M in each series do not always vary irregularly, but show a continuous increase or decrease with increasing concentration. Using α for the degree of ionisation and $k_H=463\times10^{-6}$, the five experiments

for hydrobromic acid give $k_M = 276$, 514, 575, 600, and 609×10^{-6}, and those for p-toluenesulphonic acid $k_M = 942$, 759, 713, 670, and 649×10^{-6}. In the same way, the use of a' and $k_H = 561 \times 10^{-6}$ gives, in the case of trichlorobutyric acid, the series $k_M = 570$, 534, 520, 496, and 496×10^{-6}. On this account we are inclined to attach less significance to the values of k_M and of the ratio k_M/k_H which are obtained by the use of a common value of k_H for all the acids investigated. At the same time, we must admit that no entirely satisfactory argument can be advanced against the use of this mean value. These values, calculated as already described, are shown in table VII.

TABLE VII.

$a = \Lambda/\Lambda_\infty$, $k_H = 463 \cdot 10^{-6}$ $\quad a' = \Lambda\eta/\Lambda_\infty$, $k_H = 461 \cdot 10^{-6}$.

Acid.	$k_M \cdot 10^6$.	k_M/k_H.	$k_M \cdot 10^6$.	k_M/k_H.
Hydrochloric	728	1·57	781	1·70
p-Toluenesulphonic ...	702	1·52	—	—
Trichloroacetic	602	1·30	691	1·50
Hydrobromic	565	1·22	605	1·31
Trichlorobutyric	498	1·08	511	1·11

It will be observed that the use of a common value of k_H in the calculation of the activity ratios leads to a considerable alteration in the sequence, in that hydrobromic acid and *p*-toluenesulphonic acid exchange positions. It does not seem possible, however, to discuss with any degree of profit the relative merits of the ratios in table VI and VII, but for the reason given above we prefer the values recorded in table VI.

The relations exhibited by trichlorobutyric acid are of special interest in that the coefficients of activity for the ionised and non-ionised acids are very nearly equal. In other words, the activity of this acid, as measured by the equivalent velocity of the catalysed reaction, is constant and independent of the degree of ionisation. According to measurements of the rate of esterification of weak organic acids in methyl- and ethyl-alcoholic solution under the influence of hydrochloric acid as catalyst (Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 30; Goldschmidt and Udby, *ibid.*, 1907, **60**, 728), it would seem that the same relation obtains for the activity of hydrochloric acid in these solvents. The proportionality between the activity of the acid and its concentration has led Snethlage (*Zeitsch. physikal. Chem.*, 1915, **90**, 1, 139) to put forward a theory of electrolytes which differs fundamentally from the generally accepted theory. According to Snethlage, there is no such thing as ionic dissociation, and the conductivity ratio Λ/Λ_∞ has in general no simple significance, although it affords an

approximate measure of the proportion of non-ionised active molecules in a solution.

Snethlage's interpretation of the behaviour of acids leads to the view that these may be divided into two groups. The first group contains the strong acids, the molecules of which are all chemically and electrically active. The second contains the weaker acids, which are supposed to consist partly of active molecules which are very closely similar in their properties to the molecules of the strong acids, and partly of preactive molecules which are, in general, much less active both chemically and electrically. The relative numbers of these two kinds of molecules are supposed to vary with the concentration of the solution in accordance with the dilution law.

It is not within the scope of this paper to show the untenability of the various arguments advanced by Snethlage in support of his theory, but in view of the fact that this paper deals with the acids which belong to the first group, some reference may be made to Snethlage's view that these acids are non-ionised, and that non-ionised molecules are wholly responsible for the observed catalytic effects.

This view is based on the supposition that the catalytic activity of these acids is exactly proportional to the concentration. In so far as aqueous solutions are concerned, the only experiments cited in support of this proportionality are those of Palmaer (*Zeitsch. physikal. Chem.*, 1897, **22**, 492) on the rate of inversion of sucrose under the influence of hydrochloric acid as catalyst. In terms of the dual theory, the conclusion drawn from these experiments is that $k_M = k_H$. Three years ago (*Zeitsch. physikal. Chem.*, 1913, **85**, 211) the same experiments were considered by Snethlage to show that $k_M = 2k_H$. In the meantime, McBain and Coleman (T., 1914, **105**, 1517) deduced from Palmaer's observations the relation $k_M = 1{\cdot}5k_H$. The mean value is, as a matter of fact, the only one in accord with the experimental data. The supposition that $k_H = k_M$ is actually based on the consideration of the results of experiments in which the concentration of the acid varied only from $c = 0{\cdot}01$ to $c = 0{\cdot}001$. Over this range the change in the equivalent velocity of reaction is necessarily very small, since the change in the degree of ionisation only amounts to about 2 per cent., and when the error incidental to the determination of the velocity is taken into account it is quite obvious that the observations in question cannot be legitimately employed in the derivation of the value of the ratio k_M/k_H.

The fact that the catalytic activity of hydrochloric acid, as measured by V, increases in more concentrated solutions (compare

Palmaer, *loc. cit.*) is supposed by Snethlage to be due to the interaction of the molecules of the acid, an effect which increases with the concentration in accordance with the formula

$$V = V_0 + a\sqrt[3]{c},$$

in which V_0 is the equivalent velocity at zero concentration ($c = 0$) and a is a constant. This formula is applied to the results obtained by us with hydrochloric acid as catalyst (Dawson and Powis, T., 1913, **103**, 2135), and found to be quite satisfactory.

The formula is described as empirical, but it may be readily shown that it follows at once from the general equation (1) for the dual catalytic action of acids, if we make use of the approximate relation between α and c which is indicated by the conductivity data. In the case of the strong acids, the curves which are obtained by plotting Λ against $\sqrt[3]{c}$ approximate fairly closely to straight lines, corresponding with Kohlrausch's equation,

$$\Lambda = \Lambda_\infty - b\sqrt[3]{c}$$

in which Λ_∞ is the maximum conductivity corresponding with $c = 0$. This equation may be written in the form

$$\alpha = 1 - b'\sqrt[3]{c} \quad \text{where} \quad b' = b/\Lambda_\infty .$$

By substituting for α in equation (1) we obtain

$$V = k_H + (k_M - k_H)b'\sqrt[3]{c}.$$

or, since $k_H = V_0$,

$$V = V_0 + (k_M - k_H)b'\sqrt[3]{c} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This differs from Snethlage's empirical equation only in the fact that the constant a is replaced by the product of the constants $(k_M - k_H)$ and b', and it shows, moreover, that the rate of change of the equivalent velocity with the linear concentration of the acid is equal to $(k_M - k_H)$ times the corresponding rate of change of the degree of ionsation as measured by b'.

The fact that the experimental data for the strong acids can be represented by the equation $V = V_0 + a\sqrt[3]{c}$ is therefore to be attributed to the circumstance that the conductivity varies with the concentration in fairly close agreement with Kohlrausch's equation. This relation is consequently in perfect accord with the theory of the dual nature of acid catalysis.

In conclusion, it is of some interest to compare the values of the activity ratio k_M/k_H, which have been deduced from our observations, with those derived by Taylor (*Meddel. K. Vetensk. Nobelinst.*, 1913, **2**, No. 37) and Miss Ramstedt (*ibid.*, 1915, **3**, No. 7) from measurements of the rate of hydrolysis of ethyl acetate under the influence of strong acid catalysts. Since these observers assume that the degree of ionisation is measured by $\alpha = \Lambda/\Lambda_\infty$, we

have taken our ratios from the first series in table VI. The ratio derived from Palmaer's observations on sucrose hydrolysis is also included in the table.

TABLE VIII.

Values of k_M/k_H.

Catalyst	Isomeric change of acetone.	Hydrolysis of ethyl acetate	Hydrolysis of sucrose.
Hydrochloric acid	1·64	about 2 (T.)	1·48
Trichloroacetic acid	1·38	0·355 (T.)	—
Trichlorobutyric acid	1·03	0·055 (R)	—
p-Toluenesulphonic acid	1·25	—	—
Naphthalene-β-sulphonic acid...	—	0·98 (R.)	—

The two sulphonic acids are included in the table because it is probable that, for the same reaction, there would be little difference between the values of the activity ratio for the two acids. If this view is correct, the two recorded numbers are comparable.

It will be observed that for hydrochloric acid, k_M/k_H varies comparatively little with the nature of the catalysed reaction; this is also apparently true for the sulphonic acids. In the case of the two remaining acids there is, however, a large difference between the values of the activity ratio The recorded numbers for trichloroacetic acid are in the ratio of 4:1 and those for trichlorobutyric acid in the ratio 20:1. In other words, the activity of the non-ionised acid relative to that of the hydrogen ion varies with the nature of the catalysed reaction.

The magnitude of the differences involved would seem to preclude the possibility of explaining these by errors of experiment, by differences in the assumed degrees of ionisation, or by differences in the method of evaluating the velocity-coefficients. Much further work is necessary, however, before any attempt can be made to explain the observations, and in this connexion it may be pointed out that the systematic investigation of the influence of trichloroacetic and trichlorobutyric acids on the rate of inversion of sucrose ought to yield results of particular interest.

Summary.

The catalytic activity of a series of strong acids—hydrobromic, trichloroacetic, trichlorobutyric, and *p*-toluenesulphonic—has been systematically examined by experiments on the influence of these on the rate of isomeric change of acetone. The results are interpreted in terms of the dual theory, and it is claimed that the experimental data afford further support for the view that the non-ionised, as well as the ionised, molecules of the acid act as

catalytic agents. In all cases the acids are found to be more active in the non-ionised condition, although the difference for trichlorobutyric acid is very small. The catalysing effect produced by this acid is consequently determined solely by the concentration and is independent of the degree of ionisation.

By comparison of the values of k_M/k_H with those calculated from similar observations on the rate of hydrolysis of ethyl acetate, it is found that for some acids the ratio of the activity of the non-ionised acid to that of the hydrogen ion has approximately the same value for different reactions, whilst for other acids widely different values are obtained for the ratio according to the nature of the catalysed reaction.

Some of the materials used in this research have been purchased with the aid of a grant from the Chemical Society, for which the authors desire to offer their best thanks.

THE UNIVERSITY, LEEDS. [*Received, October 23rd,* 1916.]

XCI.—*The Quantitative Absorption of Light by Simple Inorganic Substances. Part I. The Haloids of the Alkali Metals and Hydrogen.*

By PETER JOSEPH BRANNIGAN and ALEXANDER KILLEN MACBETH.

ALTHOUGH a considerable amount of work had been done in the investigation of the absorption of light by inorganic compounds, it nevertheless seemed desirable to undertake a further study of a quantitative nature, the end in view being an examination of the variation in the extinction-coefficient of the same salt of different members of the same family in the hope of establishing a relation between this value and atomic weight; and subsequently to see if a periodic relation existed when the elements were reviewed as a whole.

The outstanding work of a general nature already done is the series of qualitative absorptions recorded by Crymble (T., 1912, **101**, 266). The author here concerned himself, not so much with the variation of absorption in salts of members of the same group, as with the change in the effect when several groups were studied. From his results he concluded that the metallic elements fell into two groups, namely, those of constant valency, aqueous solutions of their salts being diactinic; and those of varying valency, the

salts of which in aqueous solution are characterised by strong absorption of the ultra-violet rays.

In the present work it is proposed to make a series of quantitative observations of the salts of the elements, dealing with them in groups. It will thus be possible to show any connexion that may exist between extinction-coefficient and atomic weight. Generalisations regarding the change in the absorption on passing from group to group may be made when sufficient groups have been examined. A Hilger sector photometer is being employed, with a high-tension spark as the source of illumination. Values of the "molecular extinction-coefficient" ($\log \frac{I}{I_0}/dc$, where I and I_0 have their usual significance, d is the length in cm. of solution through which the light passes, and c is the concentration in gram-molecules per litre) are found for particular wave-lengths. Graphs are plotted of such values against oscillation frequencies.

The Chlorides.

The absorptions of aqueous solutions of the chlorides of hydrogen, lithium, sodium, potassium, and rubidium were studied. The values are given in table I, and are graphically represented in Fig. 1.

The hydrochloric acid was the purest obtainable, and was free from chlorine. A 12N-solution was found to be of a satisfactory concentration.

The other chlorides were pure crystals, and were subjected to rigorous crystallisation before use. In all cases the strengths of the solutions were determined by titration with standard silver nitrate.

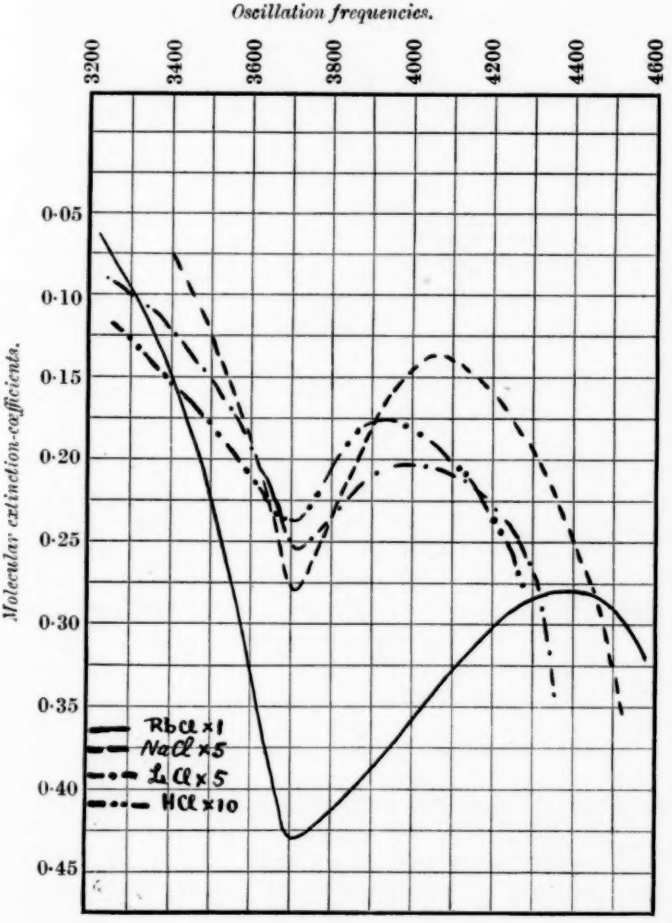
TABLE I.

Hydrochloric Acid, 4 cm. cell. 12N.		*Rubidium Chloride*, 1 cm. cell. 4N.	
λ.	$\log \frac{I}{I_0}/dc$.	λ.	$\log \frac{I}{I_0}/dc$.
236	0·0253	220	0·46
243	0·0213	221, 238, 277	0·30
250, 259, 282	0·0181	231, 279	0·28
292	0·0151	280	0·26
303	0·0121	282	0·24
315	0·0092	283	0·22
378	0·0048	284	0·20
400	0·0035	294	0·09
		310	0·06

TABLE I. (*continued*).

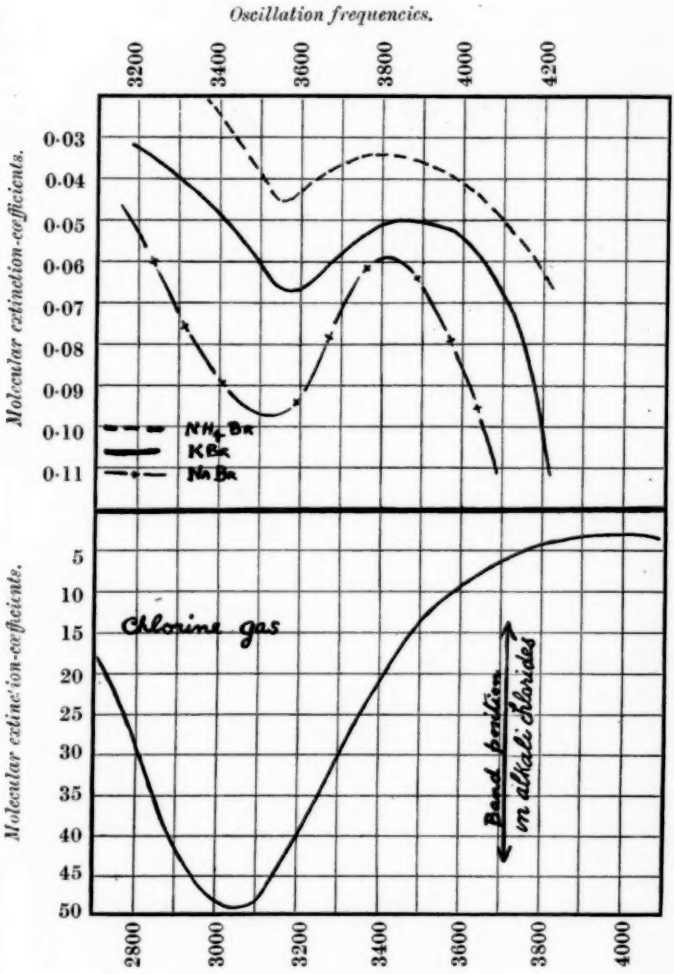
Sodium Chloride, 4 cm. cell. 4*N*.		*Lithium Chloride*, 4 cm. cell. 4*N*.	
λ.	$\log \frac{I}{I_0}/dc$.	λ.	$\log \frac{I}{I_0}/cd$.
220	0·076	229	0·076
224	0·064	230	0·064
223, 270	0·054	232	0·054
226, 273, 262	0·045	238, 261, 271	0·045
236, 278, 256	0·036	277	0·036
242, 281	0·028	293	0·028
288	0·019	300	0·019

FIG. 1.



Examination of these results shows a selective effect in these salts which up to the present have been regarded as diactinic. The band at a frequency $1/\lambda = 3730$ is persistent throughout the series of salts, and is therefore to be attributed to the common factor—the

FIG. 2.



chlorine ion. The actual cause of the band is dealt with later. The graphs also reveal an increase in the molecular extinction-coefficient with increase in the atomic weight of the metallic radicle. Lithium is an exception in this, as in so many other cases.

The Bromides.

A complete series of the bromides was not obtainable. Sodium, potassium, and ammonium salts have been studied. Purification was performed by successive crystallisations. The strengths of the solutions were determined by titration of excess silver added with thiocyanate solution. The results are set out in table II and Fig. 2.

TABLE II.

Sodium Bromide, 4 cm. cell. 2·44*N*.		*Potassium Bromide*, 4 cm. cell. 1·62*N*.	
λ.	$\log \frac{I}{I_0}/dc.$	λ.	$\log \frac{I}{I_0}/dc.$
246	0·112	236	0·172
249	0·095	237	0·146
252, 273, 304	0·080	238	0·123
257, 268, 309	0·065	239	0·100
309	0·058	241	0·080
312	0·051	249, 269, 287	0·057
316	0·044	310	0·035
325	0·037		
330	0·030		
370	0·017		

Ammonium Bromide, 4 cm. cell. 0·44*N*.

λ.	$\log \frac{I}{I_0}/dc.$	λ.	$\log \frac{I}{I_0}/dc.$
239	0.064	289	0·029
242	0.054	295	0·021
250	0.046	305	0·013
257, 269, 285	0.037		

In the bromides there is a selective effect at a frequency $1/\lambda = 3570$, and as this persists throughout the series it is evidently due to the presence of the bromine ion. The atomic weight effect is not brought out in this case, but this is not to be regarded as contradictory, as only two members of a group were examined, and these at largely differing concentrations.

The Iodides.

A full series of the iodides was obtainable and, after purification, the salts of lithium, sodium, potassium, rubidium, and cæsium were examined. The strengths of the solutions were determined by titration of excess silver added with thiocyanate solution. The values obtained are recorded in table III and are shown graphically in Fig. 3.

TABLE III.

Lithium Iodide, 4 cm. cell. $3{\cdot}10N$.

λ.	$\log \frac{I}{I_0}/dc.$
316.	0·093.
321	0·077
326	0·065
335, 349, 360	0·053
338, 350, 365	0·047
343, 366	0·041
371	0·035
374	0·030
376	0·024
378	0·019
400	0·014

Sodium Iodide, 4 cm. cell. $5{\cdot}63N$.

λ.	$\log \frac{I}{I_0}/dc.$
296	0·042
310	0·036
323, 352, 365	0·029
343, 370	0·026
378	0·023
379	0·020
380	0·017
393	0·013
398	0·010
410	0·008

Potassium Iodide, 4 cm. cell. $4{\cdot}4N$.

λ.	$\log \frac{I}{I_0}/dc.$
308, 348, 363	0·059
315, 348, 366	0·050
323, 345, 370	0·044
337, 375	0·033
382	0·018
400	0·013
460	0·007

Rubidium Iodide, 4 cm. cell. $2{\cdot}51N$.

λ.	$\log \frac{I}{I_0}/dc.$
336, 356	0·112
338, 349, 360.	0·095
366	0·080
368	0·065
370	0·058
372	0·051
374	0·044
376	0·037
383	0·030
395	0·023
400	0·011

Caesium Iodide, 4 cm. cell. $2{\cdot}03N$.

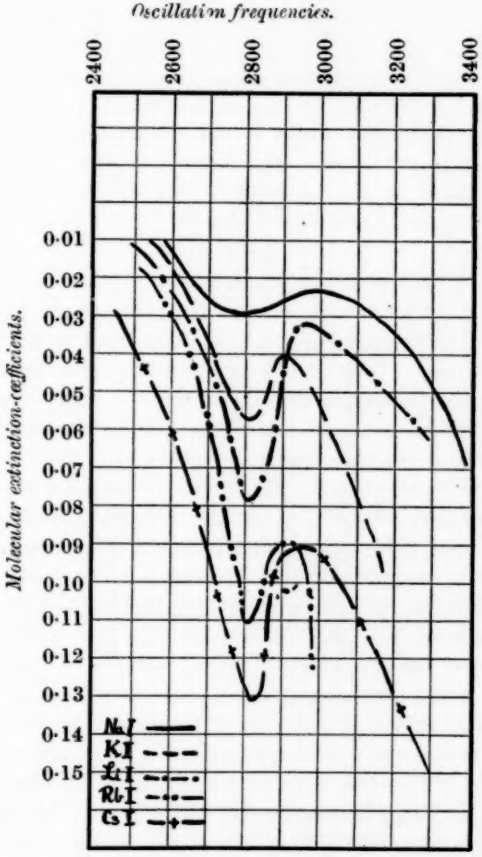
λ.	$\log \frac{I}{I_0}/dc.$
303	0·142
315, 350, 360	0·120
325, 349, 367	0·101
373	0·082
375	0·073
380	0·065
385	0·056
390	0·048
400	0·038
410	0·028
440	0·021

The selective effect due to the iodine ion is seen at a frequency $1/\lambda = 2803$. The increase in the molecular extinction-coefficient with the atomic weight of the metallic radicle is here clearly brought out, the absorption of the salts increasing continuously from sodium to cæsium. The exceptional behaviour of lithium is again in evidence, its extinction-coefficient being greater than that of sodium in the whole region examined and greater than that of potassium over the greater part of the spectrum shown.

In looking for an explanation of the selective effects obtained, it seemed advisable to examine the absorption of the free halogens

themselves. Accordingly, the spectrum of chlorine was examined, the light being passed through a 10 cm. tube having two side-tubes, fitted with taps, sealed on. One tube was connected to a source of pure dry chlorine and the other to a manometer—with an oil film to protect the mercury—an exit tube and a pressure pump.

FIG. 3.



After washing out the tube with a stream of chlorine, the exit was closed, the supply cut off, and the manometer and pump thrown into connexion. From observations of the pressure the concentration of the gas in the tube is known. A strength of 0·0021*N* was found to be suitable for work. The values are recorded in table IV and are shown in Fig. 2.

TABLE IV.

Chlorine Gas, 10 cm. tube. 0·0021*N*.

λ.	$\log \frac{I}{I_0}/dc.$	λ.	$\log \frac{I}{I_0}/dc.$
337, 324	49·0	364, 297	24·3
338, 318	45·2	368, 295	21·0
345, 313	41·4	370, 290	17·6
350, 310	38·1	210, 285, 380	14·3
355, 306	34·7	213, 280, 385	11·0
355, 304	31·0	215, 270, 400	8·1
360, 300	27·6		

Chlorine gas has therefore a strong absorption with a maximum at a frequency $1/\lambda = 3060$. The band exhibited by the chlorides has its maximum at a frequency $1/\lambda = 3730$, and it is therefore clear that the latter cannot be connected with the presence of free halogen.

The band is also not due to non-ionised chlorine in the compounds. That this is true is quickly seen from a study of the absorptions of substances containing a halogen atom which is not ionised in solution. Ethylene and *iso*butyl bromides and chlorides were examined in support of this, and gave slight general absorption only, exhibiting no peculiarities at the critical regions.

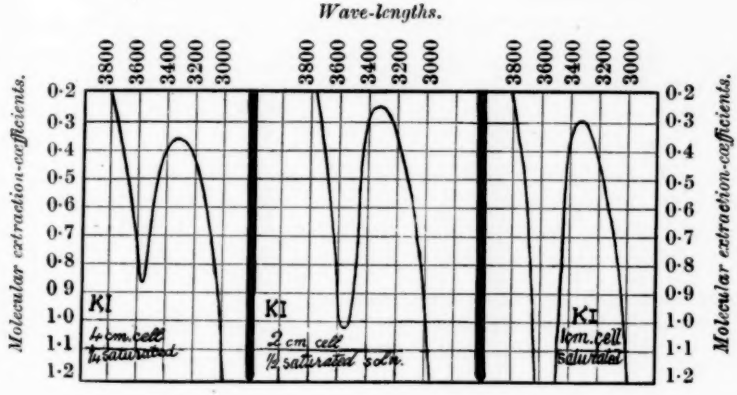
We are now driven to the assumption that the selective effects are due to the chlorine ions. If it were a simple case of these, the selective effect should be greater the greater the number of ions present. To test this, a saturated solution of potassium iodide was prepared, and portions diluted to one-half and one-quarter this strength. Absorption spectra were studied of a 1 cm. cell of the saturated solution, a 2 cm. cell of the half saturated solution, and a 4 cm. cell of the quarter saturated solution. Here we have a comparison of the absorption exercised by the same mass of salt when ionised to different degrees. The results are shown in Fig. 4. It is seen that, contrary to expectation of the simple case, the most dilute solution shows the band at least depth, the saturated solution having the band of greatest depth. The graphs in Fig. 4 are only comparative, values of $\log I/I_0$ being plotted against wave-lengths, instead of absolute values of molecular extinction-coefficient against frequencies.

From these results it would appear that the bands are not due to the free ions themselves, but are the result of vibrations set up in these by the influence of the metallic ion. The metallic ion coming within range of the acidic ion excites a vibration which is characteristic for each acidic ion, and is expressed in its absorption spectrum by a band. The frequency of the vibration depends

on the atomic mass of the halogen, decreasing as the mass of the latter increases, or, in other words, the band approaches the visible as the atomic weight of the halogen increases. In the chlorides, bromides, and iodides the frequencies are $1/\lambda$ 3730, 3570, and 2803 respectively. In the fluorides examined (sodium and potassium) no band was detected. The period of the vibration characteristic of the fluorine ion is evidently outside the range of the ultra-violet examined.

On this hypothesis of the production of the bands the results with the potassium iodide solutions meet with a ready explanation. In the more concentrated solutions the metallic ions are oftener in range of the acidic ones, and so exert a greater exciting force; the resultant vibration of the acidic ion is thereby increased in amount, with a consequent deepening of the absorption band.

FIG. 4.



Within limits, therefore, the concentration of the solution affects the penetration of the band.

It also follows from the hypothesis proposed that the mass of the metallic radicle, in members of the same group, must be a factor having a bearing on the depth of the band. The vibration excited by an ion of sodium on an iodine, or other halogen ion, would therefore be expected to be of less intensity than that produced by a heavy cæsium ion. The expression of such an effect is found on reviewing the curves. In the iodides, for example, the penetration of the bands in the cases of sodium, potassium, rubidium, and cæsium are approximately in the ratio: $\frac{3}{4}$, $1\frac{3}{4}$, $2\frac{1}{4}$, and 4.

On the grounds of the hypothesis, all metallic and acidic radicles in simple inorganic solutions should give rise to absorption bands. It may therefore be asked why no such effect was recorded to meet

the cases of the metallic radicles in this work. In answer to this, we need but to refer to the case of fluorine, where no band was obtained, although its congeners gave such decided types. The region of examination is limited, and a selective effect may well be expected in the infra-red or extreme ultra-violet in cases such as these.

Further work is being done in other groups along the lines indicated, in the hope of confirming the hypothesis and of gathering further values that may go to clear the way for any connexion that may exist between molecular extinction-coefficient and atomic weight.

Summary.

(1) The alkali haloids, which have hitherto been regarded as diactinic, are shown to exercise selective absorbing powers.

(2) The frequency of the bands decreases with increase of atomic weight of the halogen.

(3) The hypothesis that the bands are due to vibrations in the halogen ion, induced by the metallic radicle, is advanced to cover the cases examined. The vibrations thus caused may be of such frequency as to be outside the region of examination, as indicated by the case of fluorine.

(4) The molecular extinction-coefficient of the alkali haloids is shown to increase with the increase of the atomic weight of the metals, notably in the case of the iodides. The bromides do not show the effect, and lithium is abnormal.

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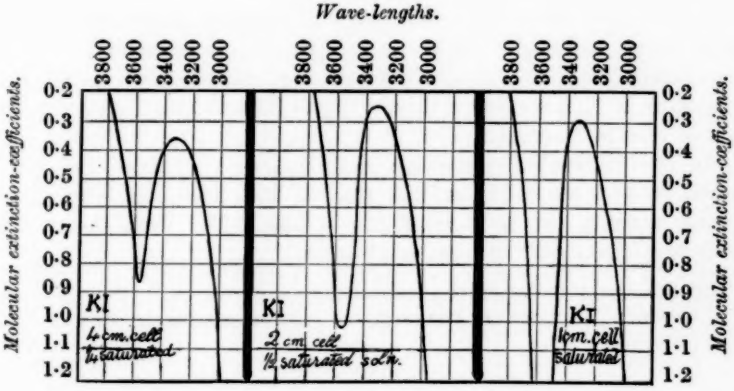
on the atomic mass of the halogen, decreasing as the mass of the latter increases, or, in other words, the band approaches the visible as the atomic weight of the halogen increases. In the chlorides, bromides, and iodides the frequencies are $1/\lambda$ 3730, 3570, and 2803 respectively. In the fluorides examined (sodium and potassium) no band was detected. The period of the vibration characteristic of the fluorine ion is evidently outside the range of the ultra-violet examined.

On this hypothesis of the production of the bands the results with the potassium iodide solutions meet with a ready explanation. In the more concentrated solutions the metallic ions are oftener in range of the acidic ones, and so exert a greater exciting force; the resultant vibration of the acidic ion is thereby increased in amount, with a consequent deepening of the absorption band.

FIG. 4.



Within limits, therefore, the concentration of the solution affects the penetration of the band.

It also follows from the hypothesis proposed that the mass of the metallic radicle, in members of the same group, must be a factor having a bearing on the depth of the band. The vibration excited by an ion of sodium on an iodine, or other halogen ion, would therefore be expected to be of less intensity than that produced by a heavy cæsium ion. The expression of such an effect is found on reviewing the curves. In the iodides, for example, the penetration of the bands in the cases of sodium, potassium, rubidium, and cæsium are approximately in the ratio: $\frac{3}{4}$, $1\frac{3}{4}$, $2\frac{1}{4}$, and 4.

On the grounds of the hypothesis, all metallic and acidic radicles in simple inorganic solutions should give rise to absorption bands. It may therefore be asked why no such effect was recorded to meet

the cases of the metallic radicles in this work. In answer to this, we need but to refer to the case of fluorine, where no band was obtained, although its congeners gave such decided types. The region of examination is limited, and a selective effect may well be expected in the infra-red or extreme ultra-violet in cases such as these.

Further work is being done in other groups along the lines indicated, in the hope of confirming the hypothesis and of gathering further values that may go to clear the way for any connexion that may exist between molecular extinction-coefficient and atomic weight.

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XCII.—*Ammoniacal Derivatives of Platinous Nitrite.*

By LEO ALEXANDROVITSCH TSCHUGAEV and STANISLAV STANISLAVOVITSCH KILTINOVIC.

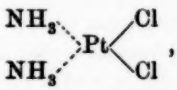
COMPARATIVELY little is known regarding the laws which govern the formation of complex compounds of cobalt, chromium, platinum, rhodium, etc., and their various reactions.

The systematic study of such reactions being of considerable interest in connexion with the constitution of complex compounds, a series of investigations on this subject, in the first instance on the compounds of platinum, was undertaken.

One of the reactions selected for this purpose was the interaction of ammonia and the complex salts corresponding with the general

formula $[PtX_4]M_2$, X being an electronegative atom or radicle and M a metallic one.

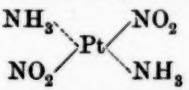
It is well known that the soluble platinochlorides, for example, K_2PtCl_4, give by the action of ammonia (if the latter reagent is not used in excess) *cis*-dichlorodiamminoplatinum (Peyrone's chloride):



together with tetra-amminoplatinous platinochloride (Magnus's green salt), $[Pt4NH_3]PtCl_4$.

A similar result is obtained if an organic amine is substituted for ammonia in this reaction.

Compounds corresponding with the general formula, $Pt2NH_3X_2$ or $Pt2AX_2$, are also formed by the interaction of ammonia or of amines and other complex salts of the type $[PtX_4]M_2$, but it has not been ascertained if they have in all cases the same *cis*-configuration. On the contrary, in the particular case of the platinonitrites, $M_2[Pt(NO_2)_4]$, first studied by Lang (*J. pr. Chem.*, 1861, **83**, 415) it was assumed that a platosammine compound, that is, an isomeride corresponding with the *trans*-configuration



is formed by the interaction of these salts and ammonia. This point was not, however, subjected to a particular and thorough examination, and therefore can by no means be considered as definitely settled.

The object of this paper is to record the results obtained by us in the study of the reactions just mentioned, and more generally in the study of the ammonia compound of platinous nitrite, $Pt(NO_2)_2$.

By the addition of ammonia to a cold solution of potassium platinonitrite a copious precipitate of very fine and nearly colourless needles is formed in a short time. The yield is almost quantitative, no other product being formed in this reaction. In complete accordance with former authors, the composition of this substance, which may be readily recrystallised from hot water, corresponds with the formula $Pt2NH_3(NO_2)_2$:

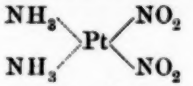
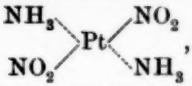
0·1495 gave 0·0913 Pt. Pt = 61·07.

0·1518 „ 24·5 c.c. N_2 at 21° and 740 mm. N = 17·79.

$PtN_4H_6O_4$ requires Pt = 60·76; N = 17·44 per cent.

In order to determine the constitution of this compound, a careful comparison with the known isomeric forms corresponding with the formula $Pt2NH_3(NO_2)_2$ or $[Pt2NH_3(NO_2)_2]_n$ was undertaken. Three

substances of this kind have been hitherto described, namely, the *cis*- and the *trans*-forms of dinitrodiamminoplatinum:

and tetra-amminoplatinous platinonitrite, $[Pt4NH_3][Pt(NO_2)_4]$, analogous to Magnus's green salt.

The first two salts were prepared for the sake of comparison by the action of sodium nitrite on *cis*- and *trans*-dichlorodiammino-platinum respectively at a gentle heat and in a slightly acidified (with acetic acid) solution. The salt, $[Pt4NH_3][Pt(NO_2)_4]$, was obtained from tetra-amminoplatinous chloride (Reiset's Base I) and from potassium platinonitrite. All these compounds were purified by crystallisation from hot water.

The comparison has shown that the substance obtained from ammonia and potassium platinonitrite was identical in its general appearance, crystalline form, colour, and other physical properties with the *cis*-isomeride of dinitrodiamminoplatinum.

The most convincing results were obtained, however, from a comparison of the solubility measurements.

At 25° the following figures (grams of substance dissolved in 100 grams of water) were obtained:

I.	II.	III.	IV.
$Pt2NH_3(NO_2)_2$ *cis*.	Substance from NH_3 and $K_2[Pt(NO_2)_4]$.	$Pt2NH_3(NO_2)_2$ *trans*.	$[Pt4NH_3]Pt(NO_2)_4$
0·083	0·082	0·063	0·011

We have further made solubility determinations of the substances II. and III. at different temperatures:

II.	25°	0·082	63°	0·66	—	—	94·5°	2·32
III.	25°	0·063	63°	0·49	74·4°	0·81	95°	1·85

It will be seen from the figure that the solubility curves are almost parallel, and that the curve corresponding with the substance II. lies distinctly higher than the curve III.

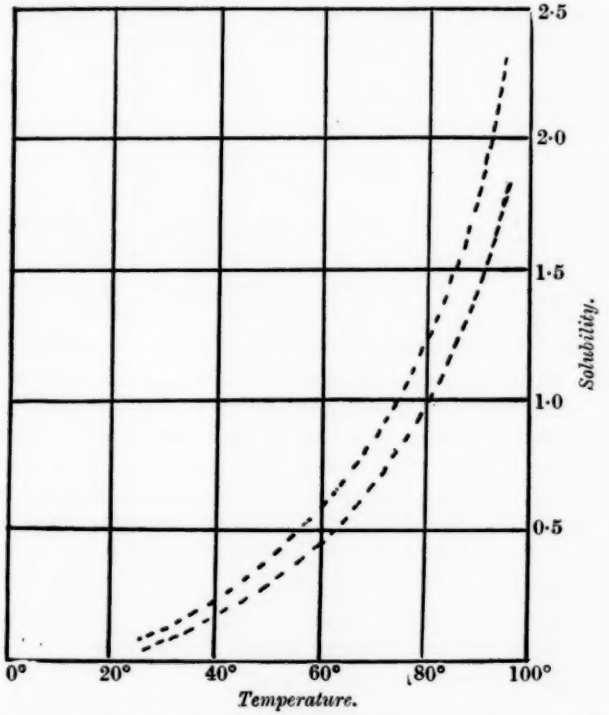
In order to obtain more evidence in favour of the conclusion that II. is identical with I. and different from III., we have determined at 25° the solubility of the two mixtures: I. + III. and II. + III.

Obviously, if I. = II. the solubility of I. + II. should be the same as the solubility of I. or of II., and, on the other hand, the solubility of II. + III. should be nearly equal to the sum of the solubilities of II. and of III. The results obtained have entirely confirmed these conclusions:

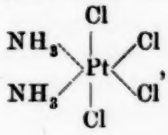
I. + II. gave 0·0817, instead of 0·083.
II. + III. „ 0·142, „ 0·146.

Although it appears very probable from these figures that the product of interaction of ammonia and potassium platinonitrite (II.) is identical with the *cis*-modification of dinitrodiamminoplatinum (I.), it seemed necessary to obtain more direct evidence in favour of the constitution of this substance, as well as of its isomerides.

For this purpose the substance II. was boiled for some time with concentrated hydrochloric acid. A green solution was produced, and a crystalline, yellow precipitate separated. After recrystallising the precipitate from boiling water acidified with



hydrochloric acid, there was obtained a yellow, crystalline substance presenting the general appearance of the well known chloride



first described by Cleve:

0·1239 gave 0·0550 Pt. Pt = 52·46.

0·1682 „ 0·2591 AgCl. Cl = 38·13.

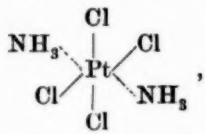
$PtN_2H_6Cl_4$ requires Pt = 52·60; Cl = 38·23 per cent.

The constitution of this compound was verified by reducing it with boiling oxalic acid in aqueous solution:

$$Pt2NH_3Cl_4 + C_2H_2O_4 = Pt2NH_3Cl_2 + 2HCl + 2CO_2.$$

After adding hydrochloric acid the solution deposited, on cooling, a copious, yellow precipitate of *cis*-dichlorodiamminoplatinum (Peyrone's chloride), giving the very characteristic reaction with concentrated sulphuric acid recently described by one of us.

The isomeric *trans*-modification of dinitrodiamminoplatinum gives similar results; the tetrachloride, $Pt2NH_3Cl_4$, which is formed from it by the action of hydrochloric acid, is identical with *trans*-tetrachlorodiamminoplatinum (Gerhardt's chloride):



and gives, on reduction with oxalic acid, the corresponding *trans*-dichlorodiamminoplatinum (chloride of Reiset's Base II.).

A very remarkable difference between the two isomeric modifications corresponding with the formula $[Pt2NH_3(NO_2)_2]$ is shown by boiling them with an aqueous solution of potassium hydrogen oxalate. With the *cis*-modification (I. or II.) a yellow solution is obtained which deposits on cooling an abundant, crystalline precipitate of the yellow complex salt, $K_2[Pt(NO_2)_2(C_2O_4)]$, first described by Vezes. This salt was identified first by its reaction with ammonia, the *cis*-isomeride, $[Pt(NO_2)_2,2NH_3]$, being again obtained under these conditions, and secondly by precipitating the solution of the yellow salt with the chloride of Reiset's Base I.

The complex salt, $[Pt4NH_3]\,[Pt(NO_2)_2(C_2O_4)]$, obtained in these reactions was recrystallised from hot water. It forms orange-yellow needles, and gave the following figures on analysis:

0·1519 gave 0·0926 Pt. Pt = 60·96.

$C_2H_{12}O_8N_6Pt_2$ requires Pt = 61·14 per cent.

Lang (*loc. cit.*) states that platosammine nitrite, that is, *trans*-dinitrodiamminoplatinum, is entirely incapable of uniting with ammonia, whereas it is well known that the corresponding chloro-derivative (the chloride of Reiset's Base II.), as well as the *cis*-isomeride (Peyrone's chloride), readily react with the same reagent to give the following compounds:

$\left[Pt\begin{matrix}3NH_3\\Cl\end{matrix}\right]Cl$ and $[Pt4NH_3]Cl_2$

Cleve's chloride. Chloride of Reiset's Base I.

It may be added that we have not been able to find any refer-

ence as to the behaviour of *cis*dinitrodiamminoplatinum towards aqueous ammonia.

In order to elucidate this point and to ascertain if there really exists such a marked difference between the chloro- and nitro-derivatives of the radicle $Pt2NH_3$ in regard to their tendency to combine with ammonia, we investigated the reactions between ammonia and the isomeric nitro-compounds, and succeeded in preparing in this way the hitherto unknown nitrite, $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]NO_2$, corresponding with the series of Cleve's salts.

Half a gram of *cis*dinitrodiamminoplatinum was heated with 15 c.c. of 8·5 per cent. aqueous ammonia and 15 c.c. of water at the temperature of the water-bath with frequent shaking. After a short time all passed in solution, and the liquid was cooled, filtered (if necessary), and slightly acidified with acetic acid. The addition of about 1 gram of potassium platinochloride dissolved in a few c.c. of water immediately produced a copious, crystalline precipitate consisting of small, glistening plates of a fine flesh colour, almost insoluble in water. The analysis of the air-dried substance gave figures corresponding with the formula of the platinochloride, $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]_2 PtCl_4$. The substance does not change in weight by heating at 100°:

0·1398 gave 0·0887 Pt. Pt = 63·45.
0·1581 „ 18 c.c. N_2 at 22° and 740 mm. N = 12·49.
0·1642 „ 0·1009 AgCl. Cl = 15·22.*
$Pt_3H_{18}N_8O_4Cl_4$ requires Pt = 63·54; N = 12·16; Cl = 15·39 per cent.

The same results were obtained by using in the above reaction *cis*dinitrodiamminoplatinum prepared from *cis*dichlorodiamminoplatinum and sodium nitrite. The corresponding platinochloride gave the following results on analysis:

0·1168 gave 0·0740 Pt. Pt = 63·37.
0·1485 „ 0·0926 AgCl. Cl = 15·43.

If *trans*-dinitrodiamminoplatinum is treated in a similar manner with aqueous ammonia at the temperature of the water-bath it also passes into solution, although not quite so readily as the *cis*-modification. The solution, after being acidified with acetic acid, was precipitated by potassium platinochloride, and the product was proved to be identical with the flesh-coloured platinochloride, $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]_2 PtCl_4$, just mentioned:

* Other analyses gave Pt = 63·36, N = 11·91. Cl = 15·45.

0·1363 gave 0·0865 Pt. Pt = 63·46.
0·1366 „ 14·7 c.c. N_2 at 22° and 755 mm. N = 12·05.
0·1464 „ 0·0905 AgCl. Cl = 15·31.
$Pt_3N_8H_{18}O_4Cl_4$ requires Pt = 63·54; N = 12·16; Cl = 15·39 per cent.

A determination was made of the solubility in water at 25° of two samples of the platinochloride in question, namely, of I, prepared from *cis*-dinitrodiamminoplatinum, of II., prepared from the *trans*-modification of the same salt, and of a mixture of I. and II.:

	I.	II.	I. and II.
In 100 grams of water ...	0·072 gram	0·077 gram	0·078 gram

As the platinochloride is not very stable in aqueous solution the agreement may be considered to be quite satisfactory.

It follows from the facts just recorded that the reaction between ammonia and the two isomeric forms of dinitrodiamminoplatinum takes place in accordance with the following equation:

$$[Pt2NH_3(NO_2)_2] + NH_3 = [Pt3NH_3,NO_2]NO_2,$$

one molecular proportion of ammonia being added and one electronegative radicle (NO_2) being simultaneously removed from the I. into the II. sphere of co-ordination. As we have seen, the existence of the complex ion, $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]^+$ can be proved by the formation of the corresponding platinochloride:

$$2\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]NO_2 + K_2[PtCl_4] = \left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]_2PtCl_4 + 2KNO_2.$$

If the original solution obtained by the action of ammonia on *cis*-dinitrodiamminoplatinum is evaporated on the water-bath for a short time and then cooled, white crystals separate, which appear to be identical with *trans*-dinitrodiamminoplatinum.

The filtrate from these crystals may be precipitated by the addition of much absolute alcohol and ether. The precipitate corresponding with the formula $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]NO_2$ forms microscopical, slender needles, and is excessively soluble in water:

0·1409 gave 0·0818 Pt. Pt = 57·65.
0·1300 „ 23·5 c.c. N_2 at 21° and 767 mm. N = 20·67.
$PtN_5H_9O_4$ requires Pt = 57·70; N = 20·71 per cent.

The nitrotriamminonitrite, $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]NO_2$, gives in aqueous solution all reactions characteristic of both the constituent ions, NO_2^- and $\left[Pt\begin{smallmatrix}3NH_3\\NO_2\end{smallmatrix}\right]^+$. It gives an intense blue coloration with an acidified solution of starch and potassium iodide, and the character-

istic precipitate of the salt, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]_2PtCl_4$, with potassium platinochloride.*

The isomeric modifications of dinitrodiamminoplatinum do not show these reactions.

A series of other derivatives containing the same complex cation, $\left[Pt\begin{matrix}3NH_3+\\NO_2\end{matrix}\right]$ may be prepared from the salt, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]NO_2$.

The *platinobromide*, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]_2PtBr_4$, is readily obtained by the addition of potassium platinobromide, K_2PtBr_4, to the nitrite, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]NO_2$. It separates in deep violet plates similar in their appearance to the platinobromide, $\left[Pt\begin{matrix}3NH_3\\Br\end{matrix}\right]PtBr_4$, recently described by one of us (T., 1915, **107**, 1247), and sparingly soluble in water:

0·1037 gave 0·0553 Pt. Pt = 53·33.

$Pt_3N_8H_{18}O_4Br_4$ requires Pt = 53·26 per cent.

The *platinonitrite*, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]_2Pt(NO_2)_4$, may be obtained in a similar manner from the compound, $\left[Pt\begin{matrix}3NH_3\\NO_2\end{matrix}\right]NO_2$, and potassium platinonitrite. It forms pale yellow needles:

0·1102 gave 0·0668 Pt. Pt = 60·62.

0·1229 „ 18·9 c.c. N_2 at 18° and 766 mm. N = 17·83.

$Pt_3N_{12}H_{18}O_{12}$ requires Pt = 60·76; N = 17·44 per cent.

It may be noted that this substance represents a polymeric (trimeric) form of the salt, $[Pt2NH_3(NO_2)_2]$.

The most remarkable property of the nitronitrite,

$$[Pt3NH_3,NO_2]NO_2,$$

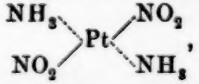
is its instability. It readily loses one molecular proportion of ammonia, even at the ordinary temperature, and much more easily at 100°:

0·1564 lost 0·074 at 100° after four hours. NH_3 = 4·73.

0·1514 „ 0·0073. NH_3 = 4·82.

Theory for $1NH_3$ = 5·03 per cent.

The product of this reaction, which takes place also in aqueous solution, was proved to be *trans*-dinitrodiamminoplatinum:



* The same nitrotriamminoplatinous nitrite may be obtained by heating the *trans*-modification of the salt $[Pt2NH_3(NO_2)_2]$ for some time with ammonia in the manner just described, and precipitating the resulting liquid with alcohol and ether.

from the general appearance of the crystals, from its chemical behaviour, for example, towards hydrochloric acid, and from the results of the solubility determinations given below.

At 25° 100 grams of water dissolved 0·065 gram of the substance (*A*) obtained from the nitronitrite by heating at 100°, and 0·066 gram of the crystals (*B*) which separated by evaporation of the ammoniacal solution of *cis*-dinitrodiamminoplatinum. In the case of a mixture of *A* with *trans*-dinitrodiamminoplatinum we obtained nearly the same value, namely, 0·0658.

It will be seen that *cis*-dinitrodiamminoplatinum may be transformed into the corresponding *trans*-modification in passing through a compound richer in ammonia, just as in the case of the corresponding chloro-compounds, but incomparably more easily.

It may be stated in general that the introduction of nitro-groups into the molecule of ammoniacal platinum can weaken in a very marked degree the linking between the platinum atom and ammonia. This may be explained by Werner's theory of co-ordination ("Neuere Auschauungen auf dem Gebiete der anorganischen Chemie," 1913).

According to Werner, the addition of one molecule of ammonia to dinitrodiamminoplatinum must cause the displacement of one nitro-group, which passes into the II., or external sphere. Now the nitro-group (like cyanogen) obviously possesses a very considerable tendency to unite immediately with the atom of platinum, in other words, to return into the I. sphere of co-ordination. For this reason nitrotriamminoplatinous nitrite, being formed in the reaction:

$$[Pt2NH_3(NO_2)_2] + NH_3 = [Pt3NH_3NO_2]NO_2,$$

is readily decomposed, with the formation of the diammino-compound:

$$[Pt3NH_3NO_2]NO_2 = [Pt2NH_3(NO_2)_2] + NH_3.$$

The former reaction is naturally furthered by an excess of ammonia, whereas the latter predominates in proportion as the concentration or the partial pressure of ammonia diminishes.

If we start from the *trans*-modification of the compound $[Pt2NH_3(NO_2)_2]$, the reaction:

$$[Pt2NH_3(NO_2)_2] + NH_3 \rightleftarrows [Pt3NH_3,NO_2]NO_2$$

becomes practically a reversible one, for the *trans*-isomeride is regenerated by dissociation of the triammino-compound, and, on the other hand, the fixation of the second molecule of ammonia, according to the equation:

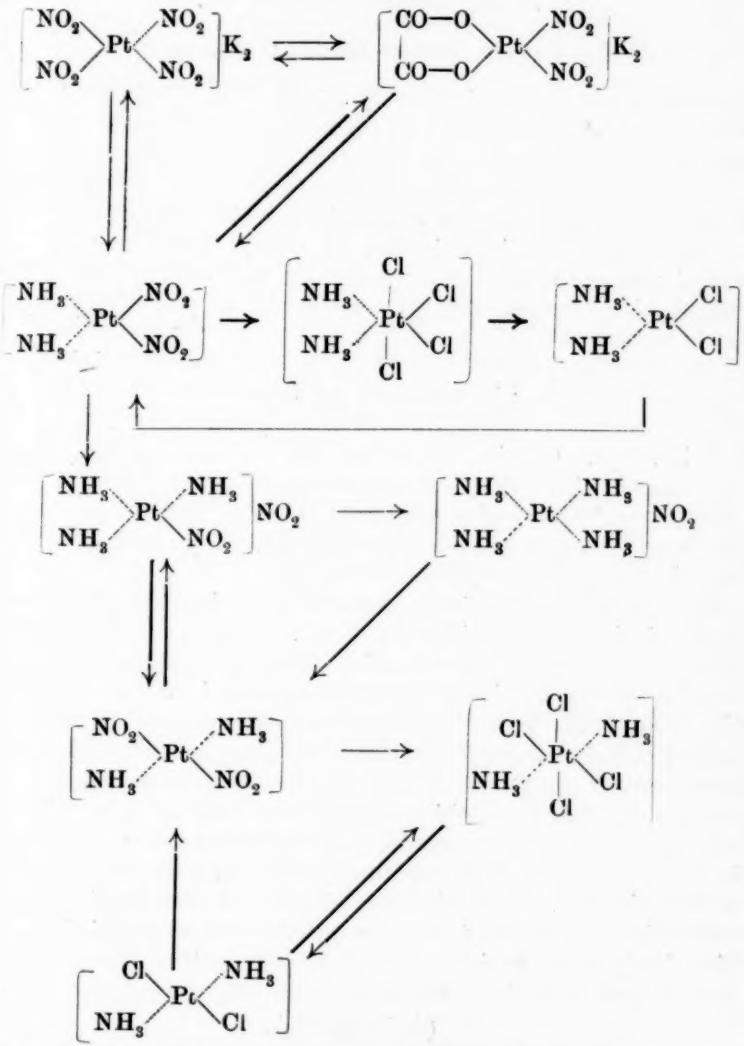
$$[Pt3NH_3,NO_2]NO_2 + NH_3 = [Pt4NH_3](NO_2)_2,$$

proceeds but slowly, especially if not too great a concentration of ammonia is used.

If, however, the initial dinitro-compound is the *cis*-modification,

the elimination of ammonia from the nitrotriamminonitrite results in an isomeric change.

The chief results of this investigation may be indicated as follows:



THE CHEMICAL LABORATORY OF THE IMPERIAL UNIVERSITY,
PETROGRAD. [*Received, August 2nd,* 1916]

XCIII.—*The Reaction between Methyl Iodide and Some Metallic Cyanides.*

By Ernald George Justinian Hartley

In some recent communications (T., 1913, **103**, 1196; 1914, **105**, 521) the author described the preparation of isomeric forms of tetramethyl ferrocyanide and trimethyl cobalticyanide respectively.

In the hope of discovering further examples of such isomerism in compcunds of a simpler constitution, which might throw light on the subject, an investigation of methyl silver cyanide and methyl mercury cyanide was commenced, and although no further instances have been observed, the results of the preliminary experiments seem worth while recording.

The Reaction between Silver Cyanide and Methyl Iodide.—This reaction has been chiefly studied by Gautier, and is one of the general methods of preparing *iso*nitriles (*Ann. Chim. Phys.*, 1869, [iv], **17**, 203). Gautier found that when silver cyanide (2 mols.) and methyl iodide (1 mol.) are heated in sealed tubes at about 100°, silver iodide and a compound, $CH_3{\cdot}NC,AgNC$, are formed, and from the latter methylcarbylamine is readily obtained by heating with a solution of potassium cyanide.

Wade (T., 1902, **81**, 1608) observed that silver cyanide absorbs methyl iodide at the boiling point of the latter, a solid substance being formed, which on heating liberates methylcarbylamine. Gautier apparently alludes to this compound in one of his papers (*Annalen*, 1868, **146**, 121), describing it as an iodocyanide of methyl and silver. Neither of these chemists, however, isolated the compound or gave any analytical data, but Wade suggests the formula Ag·NRI:C, to which objection has been taken by Sidgwick on the ground that the groups CH_3 and I would be more likely to attach themselves to the extremely active dyad carbon atom than to the nitrogen. A further examination of the reaction by the author has now shown that silver cyanide and methyl iodide combine slowly at the ordinary laboratory temperature when a crystalline compound results corresponding with the formula

$$(AgNC)_2,CH_3I.$$

At a temperature of about 40° a further molecule of methyl iodide is taken up, and the compound $AgNC,CH_3I$, or perhaps $(AgNC,CH_3I)_2$, is formed in agreement with Wade's suggestion. Experiments with potassium silver cyanide showed that this double salt was incapable of reacting with methyl iodide, no change being

noticed when the two substances were heated at 95—100° in a sealed tube for twenty-four hours.

A possible explanation of these phenomena is here suggested. Potassium cyanide, assuming it has the *iso*nitrilic formula K·N:C, contains a dyad carbon atom and a triad nitrogen atom. When addition takes place, there is a tendency for groups to add on to the carbon, rather than to the nitrogen, as, for example, on oxidation to cyanate or in the formation of ethyl cyanimidocarbonate (Nef) from potassium cyanide and ethyl hypochlorite, or, again, it is supposed that the alkyl nitriles are produced from potassium cyanide and alkyl iodide through the intermediate compound, K·N:CRI (see Cohen, "Organic Chemistry," Vol. II., p. 10).

On the other hand, in the case of silver cyanide, addition of the groups R and I seems to be to the nitrogen atom, and not to the carbon, judging by the subsequent formation of *iso*nitriles, although when the acyl haloids react with the silver salt, nitrilic, and not *iso*nitrilic, derivatives result.

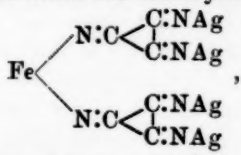
This behaviour of potassium silver cyanide and silver cyanide can be most readily accounted for by giving to these salts the following structural formulæ:

$$K\cdot N{:}C{:}N\lessdot{}^{C}_{Ag} \quad \text{and} \quad Ag\cdot N{:}C{:}N\lessdot{}^{C}_{Ag}.$$

In the potassium double salt the two free valencies of the dyad carbon atom in the K·N:C: group are saturated by the two free valencies of the nitrogen in the Ag·N:C group. The silver salt is given a similar constitution. The nomenclature potassium argenticyanide and silver argenticyanide helps to express the different functions of the metallic constituents of the molecule.

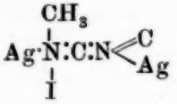
This formula accounts for the failure of methyl iodide to react with potassium argenticyanide, since the free valencies both of the carbon and nitrogen atoms, to which addition of CH_3 and I takes place, as shown above, are no longer available.

In connexion with this point, it may be remarked that certain other double cyanides containing silver, for example, silver ferrocyanide, combine readily with methyl iodide. In fact, six molecules of the latter are taken up, one being attached to each nitrogen atom (T., 1911, **99**, 1553; 1912, **101**, 706). This is quite in accordance with Browning's formula for ferrocyanides, namely,

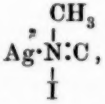


in which all the nitrogen atoms are triad.

The behaviour of silver cyanide and methyl iodide is also accounted for, the compound,



being formed at low temperatures. At a higher temperature the group



splits off, leaving the unsaturated residue, $Ag{:}\ddot{N}{:}C$ to combine further with methyl iodide, so that the whole is finally converted into the iodocyanide, as was found experimentally.

As stated above, when acetyl chloride acts on silver cyanide, nitrilic compounds are formed. Now the above structure of a silver cyanide represents it as containing a dyad carbon atom as well as a triad nitrogen, and whilst the alkyl and halogen attach themselves to the nitrogen, it must be assumed that the more negative groups, acetyl and halogen, are attracted by the free valencies of the carbon atom, rather than the nitrogen, as was, in fact, suggested by Wade (*loc. cit.*).

On the assumption of a more symmetrical structure for the argenticyanides, for example, $K{\cdot}N{:}C{:}C{:}N{\cdot}Ag$, it is difficult to account for the properties just enumerated.

Experimental.

Silver cyanide (4·83 grams), with an excess of methyl iodide, was allowed to remain for seven days at the ordinary temperature. The solid matter was then found to weigh 7·46 grams. It was very slightly yellow, and appeared under the microscope to consist of minute, rectangular prisms. The crystals were again subjected to the action of methyl iodide, and after seven more days the weight had only increased to 7·67 grams.

When examined under the microscope there was little change, but it was noticed that a few long needles had formed. The calculated weight for the compound, $(AgNC)_2,CH_3I$, is 7·41 grams. On keeping the crystals in a vacuum over sulphuric acid the needles became yellow and opaque, and there was a slight loss of weight, but the rectangular prisms remained unchanged.

On boiling with water, all the crystals became yellow and opaque, evidently with the formation of silver iodide, and the solution, which had a strong odour of *iso*nitriles, gave, with hydrochloric acid, a precipitate of silver chloride.

The compound, $(AgNC)_2,CH_3I$, apparently decomposes under these conditions into silver iodide and the compound, $AgNC,CH_3{\cdot}NC$, the latter passing into solution. On evaporating the solution over sulphuric acid, silver cyanide separated and methylcarbylamine was continuously liberated.

On heating the crystals from 100° to 150° there was a gradual loss of weight with the evolution of methylcarbylamine and the formation of silver iodide.

Silver cyanide (4·44 grams) with excess of methyl iodide was heated at about 40° for three days, when the weight of solid matter was found to be 8·85 grams. After two more days' heating with methyl iodide it had only increased to 9·00 grams, and the substance had begun to turn slightly brown.

The calculated weight, assuming the formation of the compound $AgNC,CH_3I$, is 9·14 grams.

The solid matter, when examined under the microscope, was now seen to consist entirely of long, white needles, which were extremely unstable, rapidly becoming yellow and opaque on keeping in the air or in a vacuum, and emitting an intense odour of *iso*nitriles; they keep moderately well, however, if placed in a well-stoppered bottle immediately the excess of methyl iodide has evaporated off.

The loss of weight of these crystals in an exhausted receiver over sulphuric acid was 10·3 per cent., and on heating at 100° and finally at 160°, 12·3 per cent. The calculated loss, assuming complete decomposition into silver iodide and methylcarbylamine, would be 14·8 per cent. The whole of the methylcarbylamine, however, is not given off under these conditions, but forms a small quantity of brown, non-volatile matter, which remains with the silver iodide, so that the actual loss of weight is less than the theoretical.

Two determinations of the silver iodide produced when the substance is boiled with dilute nitric acid gave 86·04 and 85·5, the calculated amount being 85·1 per cent.

These reactions were carried out several times, and always gave quite similar results, so that the formation of the two well-defined compounds, $(AgNC)_2,CH_3I$ and $AgNC,CH_3I$ or perhaps

$$(AgNC,CH_3I)_2,$$

may be regarded as proved.

The Reaction between Mercuric Cyanide and Methyl Iodide.

Calmels (*Compt. rend.*, 1884, **99**, 239) states that when these two substances are heated at 110° for half an hour a mixture of a tarry product, free mercuric iodide, and methylcarbylamine is produced.

On repeating his experiments, the author obtained somewhat different results. A black, tarry, amorphous substance was formed,

but no free mercuric iodide was observed, nor could any odour of *iso*nitriles be detected on opening the sealed tube in which the reaction had taken place.

Moreover, the weight of the black substance, although the latter was clearly not a pure compound, always agreed substantially with the formation of a definite compound, $(CH_3NC)_2,HgI_2$. For example, 9·42 grams of mercuric cyanide were heated at 95° with excess of methyl iodide until all the salt had disappeared. The black product was washed out of the tube with acetone, in which it is extremely readily soluble, and after the acetone and excess of methyl iodide had been evaporated off, the weight of solid matter was found to be 20·2 grams, the calculated amount being 20·1. The substance is soluble in acetone, forming a very dark solution, but does not dissolve readily in any other of the ordinary organic solvents or in water.

On warming with dilute nitric acid, mercuric iodide separates, and a dark red solution is obtained which yields a red, semi-solid substance on evaporation to dryness in an exhausted desiccator over lumps of sodium hydroxide. This red substance is insoluble in acetone, but readily soluble in water, and contains no mercury or iodine. On adding to the aqueous solution some solution of potassium mercuric iodide, a buff-coloured, amorphous precipitate is obtained, soluble in acetone, which is doubtless a purer form of the compound, $(CH_3NC)_2,HgI_2$. It was not, however, found possible to crystallise it or otherwise purify it further.

The black product dissolved in acetone can also be separated into its constituents by a solution of silver nitrate, silver iodide being precipitated. The mercury can then be removed by passing hydrogen sulphide, and on evaporation to dryness the same red, semi-solid substance as above described is left, the aqueous solution of which gives the buff-coloured, amorphous salt with mercuric iodide.

A determination of mercury in two samples of this amorphous solid gave Hg = 36·29 and 36·18, the calculated amount being 37·39 per cent., showing that the product is by no means pure. Owing to the fact that no *iso*nitriles could be detected in this reaction, it was thought possible that Calmels had made some error, and that the substance produced might have a nitrilic, and not an *iso*nitrilic, constitution, and this was apparently confirmed by the fact that when some of the black substance was decomposed by warming with concentrated sulphuric acid only ammonium salts were found amongst the products of decomposition, and no methylamine (compare T., 1911, **99**, 1551). In order to obtain further evidence on this point, an attempt was made to prepare it directly from its constituents. For this purpose mercuric iodide and acetonitrile were

heated together at 100° in a sealed tube, but no combination took place. An experiment was then made to see whether mercuric iodide would combine directly with methylcarbylamine.

In order to avoid first isolating the latter, advantage was taken of the compound, $AgNC,CH_3I$ (described earlier in this paper), which readily parts with methylcarbylamine on heating.

A glass tube was bent into a **W**-form, and into the bottom of one bend was placed the above silver compound, and into the other some mercuric iodide, when the tube was sealed and heated at 100°. In a very short time the mercuric iodide was converted into the black, tarry substance exactly resembling that formed from mercuric cyanide and methyl iodide, so that its constitution as a compound of methylcarbylamine with mercuric iodide is proved.

It was found subsequently that when the dark red substance obtained by decomposing the original material with dilute nitric acid is boiled with sodium hydroxide, all the nitrogen is evolved as methylamine, and not as ammonia, so that the effect of using concentrated sulphuric acid for the decomposition must have been to cause the complete destruction of the attachment of the methyl groups to nitrogen, whereby only ammonium salts were found.

Unfortunately, the red substance could not be isolated in a crystalline condition or in any form suitable for analysis or for a determination of molecular weight. It has some basic properties, forming an insoluble and unstable periodide when treated with a solution of iodine in potassium iodide. It is evidently a compound of two or some multiple of two molecules of methylcarbylamine which have combined under the influence of the mercuric iodide to form a basic substance.

The further examination of this compound has not been continued, but in the following paper other examples are given of the influence of mercuric iodide in effecting certain reactions of a somewhat similar nature.

FOXCOMBE LABORATORY,
NR. OXFORD.

[*Received, October 19th*, 1916.]

XCIV.—*Some Reactions Produced by Mercuric Iodide.*

By Ernald George Justinian Hartley.

In the preceding paper it was shown that when methylcarbylamine is heated in contact with mercuric iodide combination occurs, and there is formed the mercuric iodide of a base, which is a condensation product of two or more molecules of the carbylamine.

On the other hand, mercuric iodide and acetonitrile were shown to be incapable of reacting. When, however, mercuric iodide, acetonitrile, and methyl iodide are heated together in a sealed tube at 100°, combination takes place between the three substances, a dark brown, viscous oil being produced.

The reaction appears to be a general one, mercuric iodide and methyl or ethyl iodide combining readily under the above conditions with acetonitrile, propionitrile, benzonitrile, phenylacetonitrile, and β-naphthonitrile, the product being apparently the mercuric iodide of a quaternary base. On the other hand, when iodobenzene replaced the alkyl iodide, no combination took place.

A somewhat similar phenomenon has been observed by Smiles (T., 1900, **77**, 163, who showed that mercuric iodide accelerates the combination of alkyl sulphides with alkyl iodides, the mercuriiodide of a sulphonium base being produced.

On comparing, however, the parallel cases of the sulphides and nitriles respectively, the following differences are noticeable. First, the alkyl sulphides and iodides do combine slowly without the aid of mercuric iodide, whilst the alkyl nitriles and iodides do not react at all, at least not appreciably, on heating together at 100° for several days; secondly, the alkyl sulphides alone combine with mercuric iodide to give compounds of the general formula R_2S,HgI_2, whilst the nitriles do not appear to have any action on the mercury salt, which simply dissolves in the liquid on heating and crystallises out unchanged on cooling.

Experimental.

The mercuric iodide was in each case sealed up with excess of the nitrile and alkyl iodide, and heated at about 90—100° until it had completely disappeared. On opening the tube and evaporating off, or dissolving out the excess of nitrile and alkyl iodide, a dark, viscous, uncrystallisable oil remained, insoluble in water, but readily soluble in acetone.

On treating the acetone solution with an aqueous solution of a silver salt, the iodine was precipitated as silver iodide, and the mercury and excess of silver could then be removed by hydrogen sulphide. There was thus obtained a yellow solution containing the salt of a base combined with the acid radicle of whatever silver salt had been employed.

These salts were all readily soluble in water in cases where the aliphatic nitriles had been employed, but were much less readily so in the case of the compounds containing the aromatic nitriles, and were deposited from solution as yellow oils when the acetone had evaporated.

In no case could a crystalline product be obtained, although the chlorides, nitrates, and sulphates were all prepared and kept in the cold in an exhausted desiccator over sulphuric acid for a long time.

Sodium hydroxide, when added to a solution of any of these salts, precipitates the corresponding base as an oil insoluble in water, except in the cases where acetonitrile has been used, when the base is soluble. On extracting the liquid with ether and evaporating the latter, the base can be obtained as an oil possessing a strongly alkaline reaction.

When the base is dissolved in dilute hydrochloric acid and a solution of potassium mercuric iodide added, the mercuri-iodide of the former is precipitated no longer in the form of an oil, as when first prepared, but as a yellow, amorphous solid somewhat resembling silver iodide. These mercuri-iodides had in all cases low melting points, so that the precipitation had to be carried out with well-cooled solutions.

In the case of the compounds of aromatic nitriles, the chlorides of the bases were too insoluble in water for this treatment, and solutions of the salt in a mixture of alcohol and water were employed.

Partial analyses of the mercury salts prepared in this way show that they are not by any means pure compounds, but unfortunately no means has so far been found of obtaining them or any of the salts in the crystalline form.

The numbers found, however, taken in conjunction with the method of preparation, point to one of the two following formulæ as applying to the series:

I. $HgI_2,2RCN,R'I$ or II. $HgI_2,3RCN,R'I$.

Compound.	Found.		Calc. from I.	Calc. from II.
$HgI_2,CH_3\cdot CN,C_2H_5I$.....	Hg = 28·58		28·97	—
	I = 50·60		54·98	—
$HgI_2,C_2H_5\cdot CN,C_2H_5I$	Hg = 26·14	26·27	27·84	25·86
	27·10	25·37		
$HgI_2,C_6H_5\cdot CN,C_2H_5I$	Hg = 22·40	23·33	24·57	21·81
	I = 46·55		46·65	41·4
$HgI_2,C_6H_5\cdot CH_2\cdot CN,C_2H_5I$	Hg = 19·24		—	20·8
	I = 38·16		—	39·6

It is, of course, possible that different nitriles give compounds of a different general type, but the analytical figures so far obtained are not definite enough to afford any certain conclusion on this point.

One or two other properties of these substances may be mentioned here. In order to obtain the base, the original dark, oily product dissolved in acetone can be decomposed by an alkaline solution of sodium stannite instead of using a silver salt. The mercury is then reduced to the metal, and the base can be extracted with ether after first evaporating the acetone at as low a temperature as possible.

In whichever way the decomposition of the mercury compound is effected, there is much destruction of the base by hydrolysis and the yield is small.

All the simple salts are readily soluble in alcohol, and on adding an alcoholic solution of hydroferrocyanic acid, white or yellow acid ferrocyanides of the base are precipitated as solids which, however, it has not been found possible to crystallise.

Aqueous solutions of the salts give white, amorphous precipitates with soluble phosphomolybdates.

The reason for publishing these results * is that the influence of mercuric iodide in bringing about this reaction seems of itself to be of considerable interest, apart from the nature of the products, which, of course, require further investigation.

It was thought that the method might be applicable to other cases of a similar nature, for example, for the production of quaternary bases when their formation is prevented by the so-called "steric hindrance." One example of this kind has, in fact, been worked out.

In a previous communication (T., 1913, **103**, 1199) the author showed that α-tetramethyl ferrocyanide combined with methyl iodide at 100° giving hexamethyl ferrocyanogen iodide, $(CH_3)_6FeC_6N_6I_2$, from which other salts can be readily prepared. Of these, the acid sulphate and the platinichloride were found to

* See note at end of paper.

be very characteristic and convenient for purposes of identification.

On the other hand, β-tetramethyl ferrocyanide failed to combine with methyl iodide under any conditions.

On heating together β-tetramethyl ferrocyanide, methyl iodide, and mercuric iodide at 100°, combination takes place between the three substances, and a mercuri-iodide of hexamethyl ferrocyanogen results as a yellow substance crystallising well from hot acetone.

Its constitution as a hexamethylated compound was proved by decomposing with silver nitrate solution, filtering off the silver iodide, passing hydrogen sulphide to remove mercury and excess of silver, and evaporating to dryness, when a crystalline residue was left which gave the characteristic acid sulphate and platinichloride of hexamethyl ferrocyanogen alluded to above.

The publication of the preliminary experiments in this and the previous paper in such an incomplete state is due to the fact that the author is serving with the Army abroad, and there appears to be no prospect of an early continuation of the work.

The experiments were carried out in Lord Berkeley's laboratory at Foxcombe, near Oxford.

[*Received, October 19th*, 1916.]

XCV.—*Evidence Indicating the Existence of a New Variety of Fructose. A Reactive Form of Methylfructoside.*

By James Colquhoun Irvine and George Robertson.

More than a year ago (Irvine, Fyfe, and Hogg, T., 1915, **107**, 524) attention was drawn to the fact that glucose exists in forms other than the well-defined α- and β-modifications, and that this unexpected isomerism is dependent on the position occupied by the oxidic linking of the sugar molecule. So far as glucose is concerned, the evidence indicating the existence of these new forms is based largely on the discovery that the "γ-methylglucoside" isolated by Fischer is a mixture of two isomerides, and gives rise to a series of methylated derivatives possessing properties which are quite unique in the sugar group. Thus, members of the

"γ-glucose" series not only reduce alkaline potassium permanganate solution instantly, but, in addition, their condensation reactions, such as the formation of glucosides and *iso*propylidene derivatives, proceed with unusual facility. Conversely, the complexes thus formed are hydrolysed with extreme ease.

In view of this marked reactivity shown by γ-glucose and its derivatives, it seems probable that these compounds play a more important part in natural processes than the better known but more stable forms of glucose. Doubtless, for the most part, the varieties of the common reducing sugars which have been isolated in the pure, crystalline condition are constituted according to the butylene oxide type, and isomerides structurally similar to γ-glucose may only be obtained as individual compounds in exceptional cases. Their existence may, in fact, be only transient.

A review of the literature on the sugars discloses a surprisingly large number of facts which are not explained in terms of the theory that aldoses and ketoses react essentially as cyclic structures of a uniform type in which an oxygen atom connects four consecutive carbon atoms. A striking case in point is recently furnished by the results obtained by Hudson and his co-workers, who have shown that four crystalline galactose penta-acetates exist (*J. Amer. Chem. Soc.*, 1916, **38**, 1223). This significant discovery acquires a new importance when it is seen that, judging from the optical rotations of these compounds, they fall into two groups of pairs. One pair corresponds with α- and β-galactose and the other with the two stereoisomeric varieties of an unknown form of the parent sugar. This possibility is not overlooked by Hudson, who is engaged with further work on the subject, but it may be remarked that additional evidence pointing to the fact that galactose shows a most pronounced tendency to assume a new structural form is furnished by the results obtained in methylating the syrupy variety of methylgalactoside (Irvine and Cameron, T., 1905, **87**, 900). There is little doubt that this compound and its derivatives are allied to the members of the γ-glucose series, and a research is now in progress here in which the earlier work of Irvine and Cameron on methylgalactoside is being extended with the object of determining the constitution of the new form of galactose.

So far as can be predicted, however, fructose offers the best opportunity for the study of sugars conforming to the structural type of γ-glucose. Thus, the extreme ease with which sucrose is hydrolysed by the agency of acids places this substance in a unique position among glucosides. It may be argued that this instability may be dependent on the glucose or on the fructose fraction of

the molecule, or on both of these components. It has, however, been shown that the internal linking of the glucose constituent in sucrose is identical with that which exists in α-methylglucoside (Purdie and Irvine, T., 1905, **87**, 1022), and consequently the ready hydrolysis of sucrose cannot be attributed to the structure of the glucose component of the molecule. This result has been substantiated and extended in the course of a careful investigation (this vol., p. 1314) in which it is shown that fructose is present in the sucrose molecule in a form which is structurally different from ordinary crystalline fructose, but displays properties similar to those of γ-glucose.

In addition to sucrose, several other fructose derivatives are known which show marked instability towards dilute acids, the list including fructosemonoacetone, fructosediacetone, and methylfructoside. Each of the compounds mentioned is fully hydrolysed under conditions precisely similar to those which decompose γ-methylglucoside, and this at once suggests that a common structural relationship extends to all the cases.

As a preliminary to the complete identification of the structure of sucrose, it is evidently necessary to test the idea that fructose exists or is capable of reaction, as two definite compounds, differing in respect of the internal linking of the molecules, but similar in their capacity to form fructosides and to exist in α- and β-modifications. The simplest solution of the problem evidently lies in determining the number of methylfructosides which can be formed from fructose, and to study the properties of these compounds so as to ascertain their structures.

Work on the above lines was commenced by us fully two years ago, and although circumstances intervened which have prevented the completion of the research, the results obtained are sufficiently striking to merit description and discussion. Incidentally, much of the desired information was found concealed in results obtained in this laboratory ten years ago, but which could not be explained by the theories then at our disposal.

In his original preparation of methylfructoside (*Ber.*, 1895, **28**, 1145) Fischer found that the condensation of the sugar with methyl alcohol proceeded readily at 35° when the solution contained 0·5 per cent. of hydrogen chloride. The conditions of the reaction thus differ considerably from those which are generally necessary in the preparation of alkylglucosides where prolonged heating at 100° is usually required. Moreover, in the preparation of methylfructoside a considerable amount of unaltered sugar (or other compound capable of reducing Fehling's solution) persisted even when the reaction with the acid alcohol was greatly

prolonged. These abnormal features, together with those already mentioned, seem to place the compound in a totally different position from other alkylhexosides. From the fact that the product could not be distilled or crystallised, Fischer's methylfructoside was impure, and that several compounds were present was afterwards shown by Purdie and Paul (T., 1907, **91**, 289), who studied the optical changes which accompany the condensation of fructose with methyl alcohol. It was found that the first effect was a rapid and pronounced decrease in the lævorotation, and this was followed by a slower increase of activity until practically the initial optical value had been reached. This result was at the time very naturally interpreted as indicating that two forms (α and β) of methylfructoside were being produced simultaneously, but at different speeds. In the light of more recent views an alternative explanation seems possible in that the fructoside first produced may conceivably consist of an unstable form comparable with γ-methylglucoside, and that the final increase in rotation observed during the last stage of the reaction may be attributable to the slow conversion of this variety into a more stable fructoside possessing the normal γ-oxidic linking. Considerable support is lent to this view by the subsequent results obtained by Purdie and Paul in converting methylfructoside into tetramethylfructose. Two isomeric alkylated sugars were isolated, and as each displayed mutarotation the presumption is that both varieties existed in interconvertible forms, to which the usual expressions α and β may be attached. The equilibrium values shown by these two distinct varieties of tetramethylfructose are, however, widely different, and are compared below.

Liquid form, b. p. 142°/14 mm.	Crystalline form, m. p. 98—99°.
Permanent $[\alpha]_D$ in water $-20{\cdot}9°$.	Permanent $[\alpha]_D$ in water $-121{\cdot}3°$.

There is little doubt that the rotation quoted for the liquid form is affected by the presence, in the specimens examined, of some of the highly active crystalline sugar, as the latter was separated from the liquid isomeride. In all probability the true specific rotation for the latter compound will be found to be dextro, but, whatever its actual magnitude, it is evident that the value is abnormal. With the configuration present in normal fructose, methylation of the four non-reducing hydroxyl groups should not affect the lævorotation greatly, and should certainly not diminish it to the extent of reversing the sign. On the other hand, the value $[\alpha]_D -121°$ ascribed to the crystalline isomeride clearly indicates that the sugar is a derivative of the ordinary crystalline form of fructose, which shows the initial $[\alpha]_D -133°$. It would thus appear that the syrupy form of tetramethyl fructose corresponds

with the liquid variety of tetramethyl glucose (*loc. cit.*), and belongs to the γ-series.

In repeating Purdie and Paul's preparation of methylfructoside we used methyl alcohol which was not free from acetone, but nevertheless we have confirmed all their optical results, and the curve representing the changes involved is similar to that reproduced in their paper and shows the same minimum and maximum points, marked *B* and *C*. In the present instance, however, in experiments otherwise duplicate, the product was isolated at two different stages, one when the rotation had reached the minimum, *B*, and the other when the permanent value, *C*, was attained. By methods described in the experimental part, the essential product was isolated and fractionated in the high vacuum of the Gaede pump. The result was altogether unexpected, as in each case liquid distillates were obtained which possessed the composition and properties of a *methylfructosidemonoacetone*.

Much that has hitherto been obscure can now be explained. One form of methylfructoside evidently possesses in a marked degree the property of combining with acetone, even to the extent of abstracting the residual traces of the ketone present in the "acetone-free" methyl alcohol used by Purdie and Paul. The result is similar to that encountered by Perkin (this vol., p. 976) in the case of anhydrocryptopine, and, in the sugar group (Irvine, Fyfe, and Hogg, *loc. cit.*), is characteristic of compounds corresponding with γ-glucose. Judging from the optical study of its hydrolysis, our preparation of methylfructosidemonoacetone was quantitatively decomposed by *N*/10-hydrochloric acid at 50° to give fructose, thus disposing of the possibility that a γ-methylfructoside might be identical with γ-methylglucoside. The compound also displayed the vigorous reducing action on permanganate solution, which is one of the striking properties of γ-sugar derivatives.

With this information, it is now possible to reconstruct from Purdie and Paul's investigations a fairly complete account of the reaction between fructose and methyl alcohol. At least four isomeric methylfructosides are formed in the course of the change, which is complicated by the extreme ease with which the fructosides of the γ-type combine with traces of acetone.

Two of these fructosides would be derived from the α- and β-forms of the variety of the parent sugar now termed provisionally "γ-fructose"; the remaining two would be similar derivatives of the fructose of normal type. The ultimate evidence on which this view is based is, as already stated, the formation, from the methylfructoside mixture, of two distinct alkylated fructoses

each showing mutarotation to give different end-points. Without doubt, Purdie and Paul were severely handicapped in their work by the accidental formation of methylfructosidemonoacetone. After efficient methylation they obtained only poor yields of tetramethyl methylfructoside, whilst invariably an undistillable residue remained showing a low methoxyl content, which could not be increased. This evidently consisted of dimethyl methylfructosidemonoacetone, which failed to distil at the pressures then available. That this was the case is shown by their unpublished results and also by some of their published data. Thus, in one experiment, only a 32 per cent. yield of the fully methylated ketoside was isolated by the normal processes, but this was increased to 56 per cent. when the still residues were subjected to hydrolysis, then remethylated, and distilled. The increase of 24 per cent. obtained by this variation would, provided the above explanation is correct, demand the presence of about 0·7 per cent. of acetone in the methyl alcohol used in preparing the original methylfructoside. Analysis has shown that average specimens of "acetone-free" methyl alcohol do actually contain from 0·5 to 0·8 per cent. of the ketone.

A striking result bearing on this point was obtained by us, in that the methyl alcohol which is recovered from the methylfructoside preparation, and is thus deprived of the last traces of acetone, condenses with fructose in a different manner from that just described. No preliminary fall in lævorotation then takes place, the optical value at once increasing, so that the section *AB* in Purdie and Paul's curve is cut out. We were on the point of examining this reaction further, in the hope of isolating a methylfructoside of high lævorotation, when our work was interrupted, but there is, fortunately, no necessity to pursue this inquiry, as Hudson has, in the meantime, isolated a crystalline methylfructoside which is without doubt the expected compound (*J. Amer. Chem. Soc.*, 1916, **38**, 1216). Starting from tetra-acetyl fructose, the reducing group of the sugar was methylated by Purdie's reaction and the acyl groups were removed by hydrolysis. As was to be expected, the compound shows a higher lævorotation than fructose, and is without action on Fehling's solution. From its mode of formation, this particular fructoside is most probably derived from ordinary fructose possessing the butylene–oxide linking, and may be formulated as below:

$$OH\cdot CH_2\cdot CH\cdot[CH\cdot OH]_2\cdot C(OMe)\cdot CH_2\cdot OH \quad (\alpha \text{ or } \beta).$$
$$\qquad\qquad\quad \underline{\qquad O \qquad}$$

There are also good reasons for the belief that it corresponds with the tetramethyl methylfructoside obtained by Purdie and

Paul from crystalline tetramethylfructose. This compound showed a higher lævorotation than the parent ketose, for which $[\alpha]_D = -121{\cdot}3°$, whilst Hudson's methylfructoside ($[\alpha]_D$ $-172°$) displays a similar relation to fructose ($[\alpha]_D$ $-133°$). It would thus appear that the methylfructosides formulated above are also present in Fischer's methylfructoside.* Under the conditions of the condensation of fructose with methyl alcohol, these compounds would not react with the traces of acetone present, and would thus persist to the end of the reaction.

A structural formula has still to be found for the varieties of methylfructoside which show a low rotation, combine readily with acetone, and reduce permanganate solution. In the absence, so far, of much direct experimental evidence, views on this subject are of necessity largely speculative, but from analogy to the similar compounds in the glucose series the most probable formula is based on the ethylene–oxide type,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_2{\cdot}CH\text{--}C(OMe){\cdot}CH_2{\cdot}OH \quad (\alpha \text{ and } \beta).$$
$$\qquad\qquad\qquad\qquad\quad \diagdown\,O\,\diagup$$

Taking everything into account, there is thus clear evidence that fructose reacts as:

I. A compound containing the butylene–oxide ring and existing in two modifications, α and β. One form of the compound is strongly lævorotatory, and the equilibrium value is also lævo. The mutarotation of one variety of the crystallised sugar is in the downward sense, but the equilibrium may be altered so that upward mutarotation takes place. This type of fructose is not attacked by permanganate, should not combine readily with acetone, and should give rise to stable fructosides. It is represented by the ordinary crystalline variety of fructose.

II. A more reactive compound, hitherto unisolated, containing (probably) the ethylene–oxide ring, and capable similarly of existing in α- and β-modifications. The melting points would probably be lower than those of the isomerides in Class I, and the compounds may even be syrups. The specific rotation of these forms of the sugar when in equilibrium is doubtless low, and is probably dextro. Both the sugars and their derivatives are highly reactive, combine readily with acetone, and reduce permanganate solution. Fructosides derived from these compounds are hydrolysed by low concentrations of acids, and in this respect resemble sucrose, which is to be regarded as a derivative of this type of fructose.

* This idea has been confirmed, as D . Hudson has informed me that in the course of a research, the results of which are not yet published, he has succeeded in isolating the methylfructoside showing $[\alpha]_D$ – 172° from Fischer's methylfructoside mixture.—J. C. I.

A wide and important field of work may be opened out by the expansion of these ideas, and it is our hope to extend our experiments in this subject as soon as circumstances permit.

Experimental.

Simultaneous Preparation of Methylfructoside and the Condensation of the Product with Acetone.

Fifteen grams of finely powdered fructose, prepared from inulin and dried in a vacuum, were dissolved in boiling methyl alcohol, and the solution, after cooling, diluted with methyl-alcoholic hydrogen chloride so that the total volume amounted to 135 c.c., whilst the acid content was 0·5 per cent. It should be explained that the methyl alcohol employed was prepared from wood spirit which had been dehydrated over quicklime and fractionated repeatedly. Analysis showed that the acetone content was about 5 per cent., and this has an important bearing on the course of the reaction.

The solution was allowed to remain at the temperature of the room (about 15°), and the rotation determined at short intervals. Under these conditions very little darkening took place, and it was possible to obtain a complete polarimetric record of the optical changes which ensued. As noted by Purdie and Paul, the lævorotation rapidly diminished, the minimum value being attained in four hours. At this stage the condensation was arrested by the addition of silver carbonate, and, after filtration, the alcohol was removed by distillation under diminished pressure. A clear syrup remained, which reduced Fehling's solution vigorously. The product was then extracted by shaking in the cold with a large excess of neutralised ethyl acetate, and although the bulk of the material failed to dissolve, a colourless syrup was obtained when the ethyl acetate extract was evaporated in a partial vacuum. The syrup thus isolated had very little effect on Fehling's solution, and, after a second treatment with ethyl acetate, no reducing action was evident except after prolonged boiling with the reagent. The total soluble material was then fractionated in a high vacuum, and 1 gram of an extremely viscous, clear liquid thus obtained boiling at 135°/0·14 mm. The syrup, which might almost be described as a glass, behaved as a glucoside towards Fehling's solution, but was hydrolysed on gentle warming with very dilute acid. The compound also possessed the property of reducing alkaline potassium permanganate solution in the cold, which is characteristic of the γ-glucose series.

Found: n_d 1·4926. $[\alpha]_D^{20}$ in water $-18·2°$ for $c=2·351$.

As the amount of material did not admit of further fractionation, the analytical results were only approximate, but nevertheless showed that the product was not methylfructoside, but essentially *methylfructosidemonoacetone*:

Found: C=51·91; H=7·65; OMe=11·0.

$C_{10}H_{18}O_6$ requires C=51·19; H=7·69; OMe=13·2 per cent.

Hydrolysis of Methylfructosidemonoacetone.

Although, judging from the analysis, the above compound was not isolated in a pure condition at this stage, the hydrolysis was carried out in order to test our ideas as to its structure. The change was effected by dissolving the syrup (c=1·552) in N/10-hydrochloric acid and preserving the solution at 50°. The optical rotation quickly altered and showed significant fluctuations, which may indicate that two isomerides were present. Thus, the specific rotation at first increased in the lævo sense and subsequently diminished, thereafter increasing steadily to a constant value. Some of these observations are recorded below:

Time in minutes from start.	Specific rotation.
0	−18·2°
185	39·3
195	34·1
300	48·9
760	73·4 (constant).

The permanent value, when the concentration is corrected for the amount of hexose formed, shows that fructose is regenerated from a compound possessing the empirical formula $C_{10}H_{18}O_6$.

Preparation of Pure Methylfructosidemonoacetone.

Thirty-five grams of dry, powdered fructose were dissolved in 315 c.c. of methyl alcohol containing 0·5 per cent. of hydrogen chloride. The method of making up the solution and the quality of the methyl alcohol were similar to those already described. In this case, however, the solution was kept at the temperature of the room until no further optical changes took place. After neutralisation, the product soluble in ethyl acetate was isolated in the usual way, and, after three successive treatments with this solvent, was distilled at the Gaede pump. The main fraction (4·3 grams) boiled steadily at 170°/0·14 mm., and, on redistillation, distilled completely between 142° and 145° under a pressure falling from 0·05 to 0·02 mm.

The product was a colourless glass showing n_d 1·4882:

Found: C=51·15; H=7·80; OMe=13·06.

$C_{10}H_{18}O_6$ requires C=51·19; H=7·69; OMe=13·24 per cent.

The specific rotation in water was considerably higher than before, and was affected by change of temperature. For $c = 2{\cdot}625$, $[\alpha]_D^{20} - 85{\cdot}3°$ and $[\alpha]_D^{30} - 90{\cdot}3°$.

The compound was devoid of action on Fehling's solution, reacted in the usual way with permanganate solution, and was quantitatively hydrolysed to give fructose when heated with 0·36 per cent. hydrochloric acid at 50°.

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XCVI.—*The Constitution of the Disaccharides. Part I. The Structure of Sucrose.*

By WALTER NORMAN HAWORTH and JAMES LAW.

FEW organic compounds have formed the subject of investigation in such a variety of branches of chemistry as sucrose, and yet no conclusion has been reached enabling us to fix definitely the configuration of this sugar, or indeed of any other disaccharide. Fischer's formula, representing sucrose as a condensation complex of glucose and fructose united through their reducing groups, is the one which has been tentatively accepted, although several properties of the sugar remain unexplained. For example, the ease with which sucrose may be inverted by dilute acids finds no parallel in the whole series of disaccharides. Its rate of hydrolysis is, indeed, a thousand times more rapid than that of either lactose or maltose, whilst trehalose, which is also a non-reducing sugar like sucrose, and therefore should possess the same mode of linking through the reducing groups of the two constituent molecules of monosaccharide, is one of the most resistant of all simple sugars towards hydrolytic agents. A study of the chemical dynamics of inversion has contributed little to our knowledge of the mode of linking found in sucrose, but certain facts formerly considered to be of minor significance in the voluminous literature devoted to this change may find a new interpretation in the light of the results now communicated. A further difficulty in the case of sucrose is the failure to obtain any evidence of a stereochemical nature from the selective action of enzymes.

The new method of alkylating sugars and the improved means of purifying the products by distillation in the high vacuum of the Gaede pump (Haworth, T., 1915, **107**, 8) have considerably

diminished the numerous difficulties attending the preparation of the homogeneous methylated derivatives of the disaccharides. Some additional examples, extending the scope and applicability of these methods to cases of reducing disaccharides like lactose and maltose, will be communicated in a separate paper, where it will be shown that alkylated lactose and maltose are now readily accessible. Nearly two years ago (*loc. cit.*), the isolation of octamethyl sucrose as a pure homogeneous substance was described, and the present work, although still incomplete owing to the exceptional circumstances prevailing, is based on the simplified procedure there recommended for the provision of suitable initial material.

On the two previous occasions when Purdie and Irvine investigated the problem of the constitution of sucrose (T., 1903, **83**, 1036; 1905, **87**, 1028), a real hindrance was the uncertainty whether they were in possession of the pure octamethyl sucrose or a mixture containing incompletely methylated sucrose and also methylated hexoses, as the means at their disposal did not admit of the distillation of the methylated disaccharide, and, moreover, the preparation of this material in sufficient amount was tedious and expensive. One outcome of the present work is to confirm a result then obtained by Purdie and Irvine, namely, that the tetramethyl glucose fragment is a genuine scission product of octamethyl sucrose, and its isolation is not attributable to partly hydrolysed sucrose which had conceivably accumulated during the frequent methylations, and had consequently been converted into fully methylated hexosides.

A most significant observation now recorded of the experiments directed to the hydrolysis of octamethyl sucrose is that the change is not properly one of "inversion," since the polarimetric readings, although registering a diminution of dextrorotatory power, display no ultimate change of sign when the end-point is attained. The actual figures are:

Sugar.	$[\alpha]_D$		$[\alpha]_D$ of hydrolysed prhduct.
Octamethyl sucrose	$+66{\cdot}7°$	$\longrightarrow$	$+57{\cdot}0°$ (methylated hexoses)
Sucrose	$+66{\cdot}5$	$\longrightarrow$	$-20{\cdot}0$ (glucose and fructose)

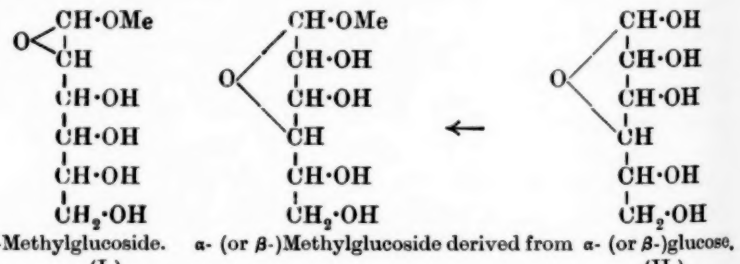
This marked difference in the magnitude of the change as compared with that resulting from sucrose must be wholly ascribed to the inherent optical characteristics of the hexoses formed during hydrolysis, as the scission products isolated were found on distillation to contain no unchanged methylated disaccharide which could have influenced the polarimetric readings in the positive direction and so masked what was, after all, a true inversion.

Speculation as to the probable end-value of the hydrolytic

change was naturally based on the known optical values of the two methylated hexoses which have already been studied, namely, tetramethyl glucose, $[\alpha]_D + 84°$, and tetramethyl fructose, $[\alpha]_D - 121°$ (Purdie and Irvine, T., 1904, **85**, 1056; Purdie and Paul, T., 1907, **91**, 296), and these rotations, quoted as equilibrium values, reveal a balance of rotation on the negative side, so that the anticipated rotation of the mixture of methylated hexoses arising from the hydrolytic change of octamethyl sucrose would be approximately $[\alpha]_D - 18°$, a result which has not been realised.

This divergence of the observed $(+57°)$ from the anticipated value has an important significance, and fortunately receives a probable explanation from other and extraneous considerations.

Attention has been directed to the remarkable ease of hydrolysis of sucrose with dilute acids, and this dilution may be even of the order $N/500$. Until recently, the only glucosidic derivative of a hexose which corresponded remotely with sucrose in the facility with which it undergoes hydrolytic change was methylfructoside. Pottevin has shown (*Compt. rend.*, 1903, **136**, 170) that, in their behaviour towards enzymes, sucrose and methylfructoside belong to the same category.* The discovery by Fischer of a new form of methyl glucoside, however (*Ber.*, 1914, **47**, 1980), and the isolation in the St. Andrews Laboratories of numerous derivatives of this new compound, have contributed a glucosidic analogue to sucrose which is hydrolysed with similar ease by the agency of acids of extreme dilution. The new glucoside (I) is considered to be a methyl derivative of a new form of glucose, namely, γ-glucose, and may be formulated alongside the ordinary modification of α- or β-methylglucoside:



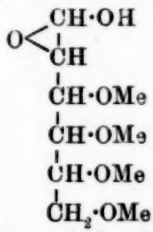
γ-Methylglucoside. (I.)

α- (or β-)Methylglucoside derived from α- (or β-)glucose. (II.)

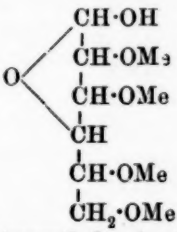
The difference between this newly isolated member of the sugar group and the previously known methylglucosides is thus attributed to a difference in structure, and certainly its exceptional proper-

* Although E. F. Armstrong appears to have interpreted Pottevin's observation in a different sense (Monographs on Biochemistry, "The Simple Carbohydrates and the Glucosides," 1912, pp. 49 and 62).

ties, such as its instability towards permanganate, necessitate this departure from the traditional views. Irvine, Fyfe, and Hogg isolated the tetramethyl γ-glucoside (III) and carefully examined its properties (T., 1915, **107**, 528). They describe it as a syrup having a lævorotation, $[\alpha]_D$ −7·21°, this being the equilibrium value in water:



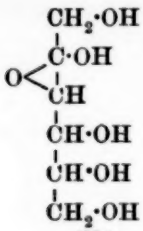
Tetramethyl γ-glucose. (III.)



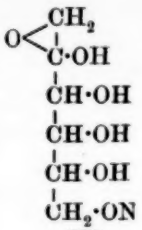
Tetramethyl α- (or β-)glucose. (IV.)

If an explanation of the irregularities noted in the results of the hydrolysis of octamethyl sucrose were to be sought in the supposition that tetramethyl γ-glucose (III) might be one of the ultimate products of scission, this would be at once negatived by two facts: first, the above tetramethyl γ-glucoside possesses a negative rotation, and therefore its appearance as one of the hexoses along with tetramethyl fructose in the product would convert the latter into a strongly lævorotatory mixture, and such is not the case; secondly, it has been established by the actual isolation of a crystalline tetramethyl glucose (m. p. 88—89°; see p. 1324) that the glucose fragment possesses the γ-oxidic structure of the normal α- or β-glucose, and thus conforms to the constitutional formula (IV).

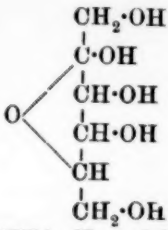
So important a development as the discovery of a new structural form of glucose naturally raises the question whether other hexoses do not also react in the γ-form, as distinct from the γ-oxidic form. For instance, why should the new formulation of a hexose not equally apply to fructose, in certain of its reactions and derivatives, as to glucose? It is seen that the essential difference in structure has reference to the ether grouping which, in a γ-oxidic form, shows an oxygen atom coupled with a chain of four carbon atoms, as in a γ-lactone, and consequently this normal form of a hexose can be regarded as a derivative of butylene oxide; whilst in the γ-form of a hexose an ethylene–oxide grouping is presumably present (III). At the present juncture, and in the absence of definite proof to the contrary, the possibility of a propylene–oxidic or amylene–oxidic structure must not be rigidly excluded. Representations of the ethylene–oxidic structure of γ-fructose (V and VI) are indicated below:



(V.)



(VI).



(VII.) Normal fructose (α or β) (butylene-oxidic).

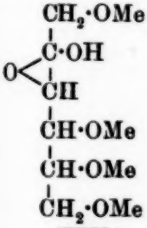
Of these two formulæ, (V) and (VI), the former is to be preferred because of its analogy to the γ-glucose formula (I), and for the present we shall adhere to this representation, although decisive proof is lacking.

Anomalous results have frequently been recorded whenever reactions have been carried out with the syrupy methylfructoside prepared according to Fischer's method, and latterly it has been shown that a pure crystalline methylfructoside can be isolated by an alternative method (Hudson and Brauns, *J. Amer. Chem. Soc.*, 1916, **38**, 1216), thus lending support to the view that Fischer's methylfructoside is probably a mixture and may contain γ-methylfructoside. Ordinarily, this would have seemed a flimsy enough basis on which to construct a theory of constitution had it not been possible to adduce evidence of an independent nature from other sources.

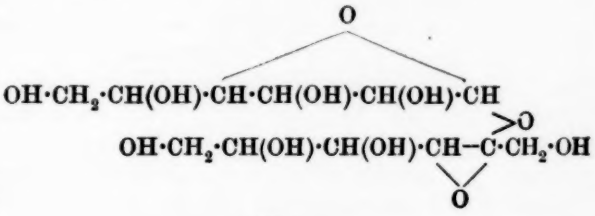
Purdie and Paul in the course of their researches on the methylation of Fischer's methylfructoside isolated a liquid tetramethyl fructose having $[\alpha]_D$ $-21°$ (T., 1907, **91**, 294), which was subsequently shown to be a composite substance containing a considerable proportion of a crystalline tetramethyl fructose melting at 98—99° and having $[\alpha]_D$ $-124{\cdot}7°$, mutarotation being responsible for the diminution of this value in aqueous solution to $[\alpha]_D$ $-121{\cdot}3°$. This activity is seen to be of the same order as fructose itself ($-140°$), exactly as the specific rotation of tetramethyl α-glucose ($+100{\cdot}8°$) is comparable with that of α-glucose ($+110°$). There can be little doubt that this is a genuine butylene–oxidic form of tetramethyl fructose, as we have found that it is quite stable to permanganate. The composite syrup from which it was derived, however, showed $[\alpha]_D$ $-21°$, and from 17 grams of this syrup 4·3 grams of purified crystalline tetramethyl fructose ($-121{\cdot}3°$) separated, that is, a proportion of approximately one-fourth of the whole. The remaining oil was found to be dextrorotatory after the strongly lævorotatory substance had been removed. It is not unreasonable to assume that in reality one-third of the original syrup consisted of the crystalline lævo-

rotatory variety, and on such a basis an approximate calculation can be made of the probable specific rotation of the pure residual liquid form of tetramethyl fructose. Using the equilibrium values quoted above for the syrupy mixture and the crystalline variety, it is found that the specific rotation of the pure liquid form of tetramethyl fructose would be $+29{\cdot}3°$ in equilibrium in water. This would then be a new form, possibly a γ-form, of tetramethyl fructose. Inserting now this value alongside the equilibrium value for tetramethyl glucose, it is seen that an equimolecular mixture of these two methylated hexoses would probably show a rotation not far removed from the mean value, which is $+57°$. It may here be recalled that the observed rotation for the hydrolysis products of octamethyl sucrose is also $+57°$, and if this is corrected for the addition of a molecule of water to the methylated sucrose, the observed value becomes $[\alpha]_D$ $+55°$, which is in close agreement with the value calculated on the above basis. Unfortunately, we have been unable to examine Purdie and Paul's liquid specimen of tetramethyl fructose, and thus cannot record its behaviour towards permanganate, but we are of the opinion, in view of the cumulative evidence adduced by Irvine and Robertson (this vol., p. 1305), that the liquid substance which Purdie and Paul had in their hands was the hitherto unrecognised tetramethyl γ-fructose (VIII).

Considerable experimental support is thus afforded for the view that the mixture of methylated hexoses arising from the hydrolysis of octamethyl sucrose consists of the ethylene–oxidic (or γ-form of) tetramethyl fructose (VIII) and the butylene–oxidic (or γ-oxidic form of) tetramethyl glucose (IV) in equal proportions, and a necessary development of these results is the proposal of a new formula for sucrose (IX):



(VIII.)



(IX.)

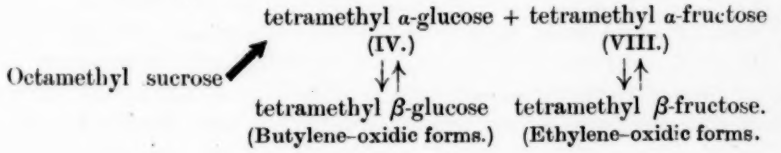
This new constitutional formula is structurally different from that originally suggested by Fischer (*Ber.*, 1893, **26**, 2400), but in his more recent paper (*loc. cit.*) the possible analogy between the structure of sucrose and the γ-type of sugars has not been overlooked. It will thus be seen that, in place of the butylene-

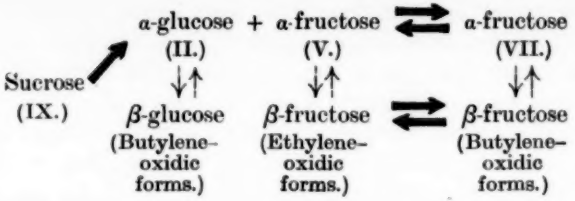
or γ-oxidic structure of the fructose half of the sucrose molecule, the ethylene–oxidic structure has been substituted, and it is evident that such a constitution best explains the exceptional properties displayed by sucrose as compared with other disaccharides particularly in reference to its ease of hydrolysis. As is well known, the facility with which an ethylene–oxide ring may be ruptured with dilute acids is so apparent as almost to suggest unsaturation, and contrasts sharply with its stability towards alkalis. It is noteworthy that sucrose has been credited with stability in the presence of alkali hydroxide at 130°; octamethyl sucrose is certainly resistant towards the action of alkalis, as it can be prepared by methylating sucrose with methyl sulphate and sodium hydroxide solution at 70°. For the sake of comparison, we have ourselves prepared some ethylene oxide and studied its behaviour with permanganate. We find that even in the cold it decolorises permanganate after an interval of two or three minutes, whether in acid, alkaline, or neutral solution, and in this respect ethylene oxide may be said to resemble the γ-hexoses which have been studied. Similarly, it is observed that the tetramethyl γ-fructose isolated from the products of hydrolysis of octamethyl sucrose reduces permanganate, and so also does a solution of the purest fructose which has first been made acid and kept for an hour and afterwards neutralised before applying the permanganate test, whilst fructose which has merely been dissolved in water displays an exceptional degree of stability and only begins to reduce permanganate after about twelve hours. There can consequently be little doubt that the ordinary form of fructose is the γ-oxidic or butylene–oxidic type, and that this undergoes transformation into the less stable modification by the agency of dilute acids.

Such considerations may serve to elucidate the recondite processes represented by the inversion of sucrose and universally quoted as the standard example of the operation of the unimolecular mass-action law. An illustration of the possible complexity of this hydrolytic change was given so long ago as 1890 by O'Sullivan and Tompson (T., **57**, 920), who discovered a "residual decrease" of rotation when the hydrolysis was suddenly arrested by adding alkali to a solution of sucrose undergoing inversion and observing that the fall of optical activity persisted for a certain period. Although other interpretations are possible, the explanation seems to be that some form of interconversion supplementary to that of the cleavage of a biose is operative. The current interpretation is that the continued change is one of mutarotation alone, and is quoted as evidence of the α-glucosidic character of sucrose, since α-glucose is considered to be undergoing

the usual transformation into the equilibrium mixture, $(\alpha+\beta)$. It does not seem to have been recognised, however, that the fructose fragment must undergo a similar transformation, and that, if β-fructose is to be regarded as the fragment liberated, then the change would be one of upward mutarotation, $-140° \longrightarrow -93°$, and thus would tend to minimise the downward effect of the mutarotation of the glucose half; on the other hand, the change from α-fructose to β-fructose would tend to augment it. Of the two alternatives, the latter seems to be favoured by O'Sullivan and Tompson's results, since the magnitude of the "residual decrease" quoted by them is considerable.

Arising out of the new structural formula for sucrose which is now proposed (p. 1319), a more reasonable explanation of the mechanism of the transformations may be given. The methylation of the hydroxyl groups in sucrose simplifies the problem of allocating specific changes to definite parts of the molecule, since those hydroxyl groups which remain in the cleavage products from the hydrolysis of octamethyl sucrose must have been precisely those groups concerned in the coupling of the two hexoses in the original disaccharide. Further, as all the hydroxyl groups exposed in sucrose are protected by methyl groups in octamethyl sucrose, the structural transformations which may occur by virtue of the unprotected groups are excluded in the case of the latter substance. Thus, by restricting the functions of the constituent molecules, derived from the process of scission, to those groups only which have participated in the previous union, it is possible to analyse the procedure involved. The change which may take place in the case of sucrose, supplementing that of hydrolysis, is the conversion of one of the hexoses from a γ-form (or ethylene–oxidic) to a γ-oxidic (or butylene–oxidic) form, whilst such a change is precluded in the case of octamethyl sucrose. Concurrently with these structural changes there must take place also the usual stereochemical transformations in which only the reducing groups are involved. It is thus possible to formulate the results of the hydrolysis of sucrose and its octamethyl derivative as follows:





The arrows in bold type represent changes involving structure, the first change being simple hydrolytic cleavage; those in light type indicate merely stereochemical interconversions. It is to be kept in view that, in addition to the already complex changes formulated in the case of sucrose for which there is experimental support, it is not improbable that the α- and β-glucoses also undergo similar transformations from the butylene–oxidic type into the ethylene–oxidic type. Consequently, we are not to regard the inversion of sucrose as the simple change which it has for so long been represented, but as one of the most noteworthy examples of a complex series of transformations which organic chemistry can furnish.

An explanation of the stereochemical configuration ascribed to sucrose in the above chart is necessary. Sucrose is here represented as being constituted of α-glucose (γ-oxidic) and α-fructose (γ-form), the "α" having a spatial significance in each case and not a structural one. No conclusive evidence is yet available on this point, but the facts appear to indicate that at least the fructose fragment, at the moment of its dissolution of partnership with glucose, must possess the α-grouping; for the first change recorded by the polarimeter when octamethyl sucrose is subjected to hydrolytic cleavage with dilute acids is a pronounced rise in rotation from $[\alpha]_D$ +66·7° to 75° or 78° during the first few minutes. As the value reached is greater than can be accounted for by assuming that tetramethyl α-glucose is instantly formed (this would not in any case cause an exaltation of the rotation of octamethyl sucrose), therefore some other highly dextrorotatory sugar must have been liberated. Since the equilibrium value for tetramethyl γ-fructose has been given as +29°, the α-modification of this ethylene–oxidic type of sugar must have a higher dextrorotation, and hence the exaltation of the optical values recorded can reasonably be attributed to the presence of the fructose constituent in this highly dextrorotatory or α-form. Later, when it has been possible to study all the forms of tetramethyl fructose, it will be a simple problem to decide whether the glucose residue is also present as the α-form. At the present stage, however, it does not seem likely that only one of the constituent hexoses is accountable for the notable rise in rotation observed.

Experimental.

Hydrolysis of Octamethyl Sucrose by Dilute Acids.

The whole of the octamethyl sucrose used was prepared by the method described in a previous paper by one of us (*loc. cit.*). Preliminary experiments indicated that hydrolysis does not occur in the cold with acids of about 0·1 per cent. concentration. At temperatures above 40°, however, hydrochloric acid of this concentration readily attacks the methylated disaccharide. After several trials it was observed that the most suitable temperature at which to conduct the hydrolytic change was from 50° to 60°, and some independent experiments were carried out at various constant temperatures within this range, using a jacketed polarimeter tube for this purpose and circulating water from a thermostat through the jacket. By taking continuous readings at the polarimeter, the course of the hydrolysis could be followed, and in general the change was complete in six to nine hours. The concentration of methylated sugar was varied from 1 to 5 per cent. and the hydrochloric acid from 0·1 to 1 per cent. In the main, the results may be represented by a logarithmic curve when the changes of rotation are plotted against the time, as the following figures will show:

Time in minutes.	$[\alpha]_D$.	Time in minutes.	$[\alpha]_D$.
0	66·7°		
15	69·5	135	59·0°
20	65·5	150	58·5
25	65·0	210	58·0
40	63·0	400	57·0
50	62·5		constant.
120	59·5		

Certain well-defined irregularities were noted, only one of which appears in the above table. This is the decided increase in rotation during the initial period of the hydrolysis. In other cases, when records were taken at a much shorter interval after contact with the hydrochloric acid, the initial reading showed the value $[\alpha]_D$ +75° and +78°, and these observations are discussed in the theoretical part (p. 1322). Again, when the change was followed by taking readings more frequently over a lengthened period, curiously fluctuating values were recorded, which do not appear to be due to varying temperature conditions. When these values are plotted on a large scale they introduce re-entrant angles into the time curves. Opportunity will be taken to study this phenomenon more closely, but it would seem that the anomaly may be attributable to the varying rates of mutarotation changes which the two methylated hexoses, liberated simultaneously, are under-

going. Occasionally these changes would appear to synchronise and at other times to be opposed, but owing to the interruption of our work, confirmation of this interesting phenomenon must be deferred.

Isolation of the Products.—When hydrolysis was complete, the acid solution was neutralised by shaking with freshly precipitated silver carbonate, filtered, and heated at 50° with animal charcoal to remove traces of silver. After filtering, the liquid was evaporated to dryness at 50—60° under diminished pressure and the residue dissolved in ether, dried over magnesium sulphate, and the ether removed by distillation. The remaining syrup was fractionated by distillation under a pressure of 1 mm.

A typical example of the procedure adopted was the following: 10 grams of octamethyl sucrose were dissolved in 0·4 per cent. aqueous hydrochloric acid of sufficient volume to make a 2 per cent. solution of the sugar, and this was heated in a water-bath maintained at 60°. The digestion was continued for eight and a-half hours, and polarimetric readings were taken at intervals. The initial reading showed $[\alpha]_D$ +66·5°, and at the end of this period the specific rotation was $[\alpha]_D$ +56°. After heating for a further two and a-quarter hours, the readings showed no diminution, and consequently the product was worked up as described above.

The result of the distillation of the syrupy product is given as follows:

Fraction (1), b. p. 118—128°/0·9 mm.
„ (2), b. p 128—135°/1 mm.
„ (3), b. p. 138—150°/1·1 mm.

Fraction (3) crystallised completely on distillation, and the second fraction crystallised partly on nucleation with a specimen of tetramethyl glucose. By draining on porous tile, the crystals were separated from traces of oil and then recrystallised from light petroleum containing a very little ether. After filtering, and drying in a vacuum desiccator, the acicular crystals were found to melt at 88—89°; no lowering of the melting point was shown when the substance was mixed with another specimen of tetramethyl glucose prepared from α-methylglucoside.

The rotation of the compound was determined in a 1 per cent. aqueous solution, when the mutarotation effect characteristic of tetramethyl α-glucose was observed, the specific rotation after five minutes being +95·6°, falling to the permanent value of +83·7° after five and a-quarter hours.

Analytical results were obtained as follows:

Found: C=50·76; H=8·66; OMe=54·0.

$C_{10}H_{20}O_6$ requires C=50·85; H=8·47; OMe=52·54 per cent.

The methylated hexose isolated in the crystalline form from the second and third fractions is therefore identified as tetramethyl α-glucose (Formula IV, theoretical part).

Fraction (1) failed to crystallise on nucleation with (*a*) tetramethyl α-glucose, or (*b*) tetramethyl fructose of the normal or butylene–oxidic type, but remained as a slightly viscid oil. It decolorises permanganate after the lapse of several minutes and behaves generally like the ethylene–oxidic form of tetramethyl glucose (III) (see p. 1317). Its boiling point is also similar to that of the last-named compound, but the oil is dextrorotatory. There can therefore be little doubt that this substance is identical with the ethylene–oxidic or γ-form of tetramethyl fructose (VIII) prepared by Purdie and Paul, and described on p. 1319. Conclusive proof on this point will be available when our experiments on the preparation of Purdie and Paul's compound can be resumed. Direct comparison of all the properties of the substance will then be possible. In the meantime, we are able to report that the resemblances are so close as to suggest identity.

Thanks are due to the Carnegie Trust for a Scholarship which has enabled one of the authors to take part in this investigation.

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XCVII.—*The Preparation of Cyanamide from Calcium Cyanamide.*

By EMIL ALPHONSE WERNER.

ALL the methods which have hitherto been recommended for the preparation of cyanamide from the calcium derivative suffer from a similar serious disadvantage. The preliminary stage in every case leads to the production of a more or less concentrated aqueous solution of cyanamide, the evaporation of which at a moderate heat even in a vacuum is a decidedly tedious operation. This, moreover, is accompanied by much loss of cyanamide, as a result of polymerisation, particularly if the solution is allowed to become even faintly alkaline (compare Morrell and Burgen, T., 1914, **105**, 588, and the author, T., 1915, **107**, 720). Poor yields of cyanamide, in consequence, have been obtained; thus, from 100 grams of commercial calcium cyanamide a yield of 10 grams of

cyanamide has been considered a good result. This, as a matter of fact, is less than half of the theoretical, even from a specimen of calcium cyanamide below the average quality.

In a recent communication (*loc. cit.*) it was shown that cyanamide is very stable in the presence of acetic acid, and advantage has been taken of this in devising a process for its preparation from the calcium derivative, whereby the tedious process of evaporation has been completely eliminated and a nearly theoretical yield of cyanamide easily obtained.

The details of the method may be best described by giving the results of an actual experiment as carried out with a sample of crude calcium cyanamide, 1 gram of which was neutralised by 1·2 grams of pure acetic acid. An assay of the sample showed the presence of the calcium compound in proportion equivalent to 28·8 per cent. of pure cyanamide.

To 125 grams of pure acetic acid, diluted with 120 grams of water in a large mortar, 100 grams of calcium cyanamide, in portions of about 15 grams, were gradually added with constant stirring. When about four-fifths of the calcium cyanamide had been added, the product was a rather thick, pasty mass; it was necessary at this stage to use a pestle in order to secure thorough mixing when the last portions of the calcium cyanamide were added.

Throughout this operation, which occupied about thirty-five minutes, the temperature did not rise above 55°, and external cooling, by standing the mortar in cold water, was found quite sufficient.

After the pasty material had been well kneaded, and the calcium cyanamide thoroughly neutralised, the product was allowed to remain exposed to the air for twenty-four hours, at the end of which time it had become a friable and easily pulverisable solid. The coarsely powdered product was transferred to a Soxhlet apparatus, and extracted six or seven times with ether in the usual manner. The ether extract, which was almost colourless, was concentrated by distillation at a gentle heat, and finally evaporated to dryness in a desiccator over sodium hydroxide.

The weight of cyanamide obtained was 27·2 grams, a yield equal to 94·4 per cent. of the theoretical.

In another experiment, from 100 grams of a sample of calcium cyanamide which contained 25·2 per cent. of available cyanamide, 24·1 grams were obtained, equal to 95·6 per cent .of the theoretical.

Whilst the assay of the calcium cyanamide is not a necessary part of the process, the following points must be carefully observed in order to secure a successful result.

Having accurately determined the neutralising power of the calcium cyanamide towards acetic acid, a small excess of the latter should be taken in order to ensure that the product, before extraction with ether, shall be faintly acid throughout. If the pasty mass, as the result of imperfect mixing, be allowed to remain alkaline in parts, the ether will be found to extract a dark brown colouring matter (derived from the carbonaceous material present in crude calcium cyanamide), the removal of which is very troublesome and entails much loss of cyanamide. Should the pasty product, after exposure to air for the stated period, fail to have assumed a sufficiently dry condition suitable for extraction with ether, this can be remedied by the addition of powdered pumice, or, better still, of coarsely powdered anhydrous sodium acetate.

A very good yield of cyanamide has also been obtained from the sodium derivative in a similar manner.

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[*Received, November 7th*, 1916.]

XCVIII.—*Theory of Vegetable Tanning.*

By HENRY RICHARDSON PROCTER and JOHN ARTHUR WILSON.

IN spite of the fact that theories of tanning have formed the subject-matter of numerous controversies, no completely satisfactory theory has yet been promulgated, which is probably due largely to the lack of quantitative formulæ governing the supposed actions. It was in the hope of throwing light on the complicated phenomena of the tanning process that work was begun by one of us some eighteen years ago, on the action of dilute acid and salt solutions on gelatin. Since this time the work has steadily progressed, and mathematical formulæ have been derived governing the various parts of the tanning process. The theoretical development of this work is given in the following publications:

1. "The Action of Dilute Acids and Salt Solutions on Gelatin," by H. R Procter, *Koll. Chem. Beihefte*, 1911, **2**, 243; *J. Amer. Leather Chem Assoc.*, 1911, 270.
2. "Colloid Chemistry and Tanning," by H. R. Procter, *Gedenkboek van Bemmelen*, 1910; *J. Amer. Leather Chem. Assoc.*, 1911, 23.
3. "The Equilibrium of Dilute Hydrochloric Acid and Gelatin," by H. R. Procter, T., 1914, **105**, 313.
4. "The Acid-Gelatin Equilibrium," by H. R. Procter and J. A. Wilson, this vol. p. 307.

5. "The Swelling of Colloid Jellies," by H. R. Procter and J. A. Wilson, *J. Amer. Leather Chem. Assoc.*, 1916, 399.
6. "Theory of Colloids," by J. A. Wilson, *J. Amer. Chem. Soc.*, 1916, **38**, 1982.

In these papers, by a process of generalisation, the authors have derived quantitative equations which explain the swelling and contracting actions of electrolytes on colloid jellies, as well as the various effects of adding electrolytes to sols. In fact, the derived formulæ apply to the whole colloid state, and therefore should in themselves offer a quantitative explanation of the mechanism of tanning, which is the object of the present paper.

The tannins dissolve in water forming colloidal sols, in which the individual particles are negatively charged, so that, according to our theory, the surface layer of solution immediately surrounding the particles (which we shall hereafter designate merely as the surface layer) must contain a certain concentration of positive ions bound by electrochemical attractions to the negatively charged tannin. The tannin may acquire its charge by combining with a negative ion or by ionising, as do soaps or Congo red; it is immaterial to the theory whichever is the case. Call the concentration of tannin particles $[T']$ and that of the positive ions bound by electrochemical attractions to the tannin $[M^+]$, and let some of the electrolyte MN be added to the solution. In the surface layer there will be a certain concentration of M^+ bound by electrochemical attractions to the tannin, as well as some M^+ and N' not so bound, so that in this layer $[M^+]$ and $[N']$ will be unequal, whilst in the bulk of solution they will necessarily be equal, a condition to which Donnan's work on membrane equilibria (*Zeitsch. Elektrochem.*, 1911, **17**, 572) is applicable.

When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, that is, no work will be done. The change here considered is the transfer of δn moles of M^+ and N' from the bulk of solution to the surface layer. The work which equals zero is

$$\delta n RT \log \frac{[M^+]_I}{[M^+]_{II}} + \delta\eta RT \log \frac{[N']_{II}}{[N']_I} = 0.$$

(where $[M^+]_{II}$ represents concentration of M^+ in the bulk of solution and $[M^+]_I$ its concentration in the surface layer, whence

$$[M^+]_{II} \times [N']_{II} = [M^+]_I \times [N']_I,$$

from which it follows that if only binary electrolytes are present, the products of concentration of any pair of diffusible and oppositely charged ions will be equal in surface layer and bulk of

solution. In order to keep the mathematics as simple as possible only binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include ions of any valency; for example, if the electrolytes MN_x were present, then at equilibrium

$$[M^{x+}]_{II} \times [N']_{II}{}^{x} = [M^{x+}]_{I} \times [N']_{I}{}^{x},$$

Since any special case can readily be worked out algebraically, no useful purpose would be served by complicating the reasoning with higher equations.

The following system of notation has been adopted to keep the reasoning as closely allied as possible to that of our earlier papers (*loc. cit.*).

In the bulk of solution let

x = concentration of positive or negative ions.

In the surface layer let

y = concentration of negatively charged, diffusible ions;

z = concentration of positively charged ions bound by electrochemical attractions to the tannin.

$\therefore\ y+z$ = concentration of positively charged ions.

From the law of equality of products just derived

$$x^2 = y(y+z).$$

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan (*loc. cit.*) as follows:

$$E = \frac{RT}{F} \log \frac{1}{\lambda}.$$

But in our special case

$$\lambda = \frac{y}{x} = \frac{-z + \sqrt{4x^2+y^2}}{2x}.$$

We may therefore write

$$E = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}},$$

where z is either constant or has a limiting maximum value, and hence

$$\lim_{x = \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0.$$

proving that the potential difference existing between surface layer and bulk of solution will diminish as the concentration of electrolytes in the solution is increased. When this difference of potential has been made sufficiently small, by the addition of electrolytes, a condition is established which is favourable to the

coalescence of the particles, and consequently the tannin precipitates.

It is now necessary to refer to the papers dealing with colloid jellies (*loc. cit.*). Because of the different distribution of ions, a difference of potential must exist between the colloid jelly and the surrounding solution. When a hide is immersed in an acid solution, a highly ionisable salt of collagen is formed in which the collagen is positively charged, and therefore this potential difference will be expressed by the formula

$$E = \frac{RT}{F} \log \frac{-z + \sqrt{4x^2 + z^2}}{2x}.$$

where E is obviously of opposite sign to that in the case of tannin. In alkaline solution hide substance reacts with the resulting formation of ionisable salts, the collagen becoming negatively charged, in which case E would have the same sign as in the case of tannin.

It now becomes evident that if a hide is immersed in a slightly acid solution of tannin, as the tannin particles approach the substance of the hide, *electrical neutralisation with the resulting co-precipitation of the two colloids must follow.* This is the fundamental action of vegetable tanning. Various tannins, however, differ chemically from one another, and consequently all would not produce the same value for z under a fixed set of conditions. The greatest difference of potential between surface layer and bulk of solution will be found in those tannins in which z has the greatest value. Such tannins would combine most rapidly with the hide and form the most stable leather, but would clearly not be suited for use excepting with hide which had been almost completely tanned. A table giving the values for z for the various known tannins under a fixed set of conditions would certainly be of great value, and it is hoped that these determinations may soon be made.

The rate of tanning will be a maximum for a given concentration of liquor when the potential differences are of opposite signs and the absolute value of each is a maximum. As the concentration of electrolytes in the solution is increased, the potential differences between the solution and both the jelly phase of the hide and the surface layer surrounding the tannin particles will decrease, lessening the rate of tanning; but if the concentration of electrolytes is increased sufficiently, the tannin must precipitate alone and the collagen shrink to a hard mass. In alkaline solutions both colloids have negative charges, and consequently will not combine, while in the presence of lime the negatively charged

tannin particles are neutralised by calcium ions and a calcium compound of the tannin precipitates.

This reasoning clears up many points concerning the question of the function of acids in tan liquors and points out the important rôle played by salts, and appears to have almost infinite possibilities of extension in many industrial problems as well as in pure colloid chemistry. It is, for instance, obvious that the equations given are applicable without change to many, if not all cases of dyeing, and offer a full explanation of the functions of acids, or (with change of sign) of bases, and of neutral salts in these operations. It is also evident that the same laws are active in regard to the mineral tannages and the mordanting of fabrics, but as these are complicated by both chemical and colloidal changes it seems best to defer their consideration.

Summary.

It is shown that the combination of tannins and hide fibre, and the effect of acids and neutral salts in the tanning process, is explained by the existence of the electric potentials which Donnan has described and explained under the name of "membrane potentials." Equations are given with regard to the relation of the various concentrations involved, and it is mentioned that these are also applicable to dyeing.

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[*Received, October 25th*, 1916.]

XCIX.—*The Hydrolysis of Iron Ammonium Alum.*

By WILLIAM NORMAN RAE.

A LARGE amount of work has been carried out with the object of investigating the composition of solutions of iron salts, but the particular case of iron alum does not appear to have been examined.

Foussereau (*Compt. rend.*, 1886, **103**, 42) found that the conductivity of ferric chloride solutions increased with time, and considered the increase to be due to hydrolysis producing hydrochloric acid and ferric hydroxide. Antony and Giglio (*Gazzetta*, 1905, **25**, ii, 1) suppose that the increase of colour of ferric chloride solutions with time is due to the formation of basic chlorides, which ultimately change to ferric hydroxide. Goodwin

(*Zeitsch. physikal. Chem.*, 1896, **21**, 1) drew the same conclusion from a study of the conductivity and colour. Spring (*Rec. trav. chim.*, 1897, **16**, 237) considers that ferric chloride is first converted into ferrous chloride and chlorine; the latter then reacts with water to form hydrochloric acid and oxygen, and this unites with the ferrous chloride to form a ferrous oxychloride, Fe_2Cl_4O. Donnan and Bassett (T., 1902, **81**, 939) suppose the colour of ferric chloride to be due to a complex, yellowish-brown anion, the ferric ion being very pale yellow.

Antony and Giglio (*Gazzetta*, 1896, **16**, i, 293) state that ferric nitrate on hydrolysis does not give a basic salt, but salts of pyro- and ortho-nitric acids, $H_4N_2O_7$ and H_5NO_5; further hydrolysis produces ferric hydroxide. They found that ferric sulphate first produces basic salts and then ferric hydroxide, which is also the composition of the precipitate. Recoura (*Compt. rend.*, 1903, **137**, 118) says that in the presence of sulphuric acid ferric sulphate gives a white precipitate, $Fe_2(SO_4)_3,H_2SO_4,8H_2O$; this is decomposed by water, and is called ferrisulphuric acid. Later (*Compt. rend.*, 1904, **140**, 1685) the same author states that with solutions containing 1 molecule of ferric sulphate to 15 of water, a basic sulphate, $7Fe_2O_3,18SO_3$, is obtained, but not when the amount of water is increased to 28 molecules. Wells (*J. Amer. Chem. Soc.*, 1909, **31**, 1027) made conductivity measurements on ferric sulphate, and found that a change took place in two steps, the first rapid and the second slow; the latter resulted in the precipitation of a basic sulphate of indefinite composition.

Iron Ammonium Alum.—Solutions of iron ammonium alum in water give a precipitate on keeping, owing to the reaction of the ferric sulphate with the solvent; the presence of ammonium sulphate increases the hydrolysis.

The time of appearance of the precipitate is found to depend on the concentration of the solution, the temperature, and the presence of other substances. In aqueous solution, a turbidity appears in one or two minutes with the most dilute solutions, whilst more concentrated ones remain clear for months. With a solution of given concentration, a rise of temperature favours rapid precipitation. The addition of ammonium sulphate increases the ease of precipitation, whilst sulphuric acid has the opposite effect.

That the precipitate is not due to the action of alkali derived from the glass vessels used is shown by the fact that similar results are obtained in quartz vessels.

The changes in colour which occur on dilution or on the addition of other substances are very noticeable; the action has therefore

been studied by means of colour measurements made under various conditions. The added substances used were sulphuric acid, since it is one of the products of hydrolysis; ammonium sulphate, as one of the constituents of the salt; potassium chloride, as a neutral salt; and sucrose, as a non-electrolyte.

Composition of the Precipitate.—The mixed precipitate from a number of solutions was filtered, washed, and allowed to dry in the air; it cannot be dried by heating, because this causes loss of the sulphuric acid which is present. The air-dried precipitate was dissolved in hydrochloric acid; the iron having been precipitated as hydroxide, the sulphuric acid in the filtrate and washings was separated as barium sulphate. The results obtained show that the precipitate approximates to the composition $2Fe_2O_3,SO_3$.

1·0189 Grams of the air-dried precipitate gave 0·5622 Fe_2O_3 and 0·3658 $BaSO_4$ (=0·1254 SO_3); since the amount of water in the air-dried substance is variable, the results are calculated on the anhydrous substance; this contains Fe_2O_3=81·8 and SO_3=18·2 per cent. The above formula requires Fe_2O_3=80·0 and SO_3=20·0 per cent.

In order to determine whether the composition of the precipitate depends on the concentration of the solution or on the temperature, precipitates were prepared and analysed as follows:

Precipitate produced by boiling a concentrated solution for 30 minutes	Fe_2O_3=82·5	SO_3=17·5
Precipitate from a cold dilute solution remaining for 24 hours.....	,, 82·6	,, 17·4
Precipitate from a cold concentrated solution remaining for two weeks	,, 80·3	,, 19·7

In each case the amount of SO_3 is low, but there does not appear to be any large variation in the composition; the low results may be due to the precipitate being decomposed by water; this was tested by treating the precipitate with cold water and by boiling; after two weeks the precipitate was found to contain SO_3=11·3 and Fe_2O_3=88·7 per cent.; water thus slowly decomposes the precipitate. The colour of the precipitate is a pale yellowish-brown, but on prolonged boiling with water changes to the familiar reddish-brown of ferric hydroxide.

When concentrated sulphuric acid is added in sufficient amount to a dilute solution of iron ammonium alum, a white precipitate separates on keeping; with more concentrated solutions of the alum the precipitate separates at once. Some of this was filtered through glass wool and washed with glacial acetic acid until the filtrate was free from sulphuric acid. The white powder was kept in the air until it was quite dry and free from odour. With cold water it passes into solution very slowly; it easily dissolves in

hot hydrochloric acid, and on boiling with water gives a precipitate similar to the basic sulphate. In air it is quite stable. On analysis it was found to be anhydrous iron ammonium alum, the ratio found for Fe_2O_3 to SO_3 being 1:4·06; the ammonia could not be estimated in the same sample, and gave a slightly low result. This precipitate might also be regarded as the ammonium salt of Recoura's ferrisulphuric acid, which was obtained in the same way.

Colour Measurements.—The colour of iron alum solutions is very considerably affected both by dilution and by the addition of substances themselves colourless. Generally, the intensity and the nature of the colour are found to be affected. The absorption bands of a number of solutions each containing 0·04 gram of the hydrated alum per c.c. were examined in a qualitative manner.

When nothing else was added, the absorption band covered the whole of the violet and the blue of the spectrum. The addition of sucrose, potassium chloride, ethyl alcohol, or ammonium sulphate caused the band to widen so as to include some of the green; the magnitude of the effect was in the order given above, being greatest in the case of ammonium sulphate, where half of the green was obscured.

In 0·1*N*-sulphuric acid the band covers half of the violet; by adding ammonium sulphate to the acid solution the band could be again widened so as to include all the blue.

Of the substances examined, therefore, sulphuric acid displaces the absorption in the direction of the violet, whilst all the other substances displace it towards the red, the greatest effect in this direction being obtained with ammonium sulphate.

Measurements of the intensity of the colour were made with a Duboscq colorimeter, using diffused daylight reflected from a white porcelain plate as the source of light. Whenever possible the colour was compared with that of a brown tinted glass plate; when it was not possible to make the comparison directly (owing to the faintness of the colour), comparison was made with an iron alum solution which had been compared with the plate, and the colour was then calculated in terms of that of the plate; determinations made in this way were less accurate, and are marked with an asterisk. Each colour value was deduced from the mean of six determinations of the colour; the actual readings are shown in one case (table I); in other cases only the calculated value of the colour is given.

TABLE I.

Colour in the Presence of 1·0N-*Ammonium Sulphate* (66 grams per litre).

Iron alum, gram per c.c.	Colorimeter readings in cm.	Mean.	Colour.
0·008	2·62, 2·69, 2·70, 2·67, 2·67, 2·68	2·67	37
0·020	1·40, 1·34, 1·34, 1·33, 1·32, 1·40	1·36	74
0·035	0·99, 0·92, 0·94, 0·93, 0·96, 0·91	0·94	106

In the first case, the mean reading of the colorimeter is 2·67, that is, 2·67 cm. of the solution balance the colour of the plate; the colour intensity of the solution is inversely proportional to the depth of it required to match the colour of the plate; the colour of the solution in terms of that of the plate can therefore be obtained by taking the reciprocal of the colorimeter reading. When the reading is 2·67 the colour is $1/2{\cdot}67 = 0{\cdot}37$; this value is multiplied by 100 to avoid decimal values. The general results obtained are shown in table II.

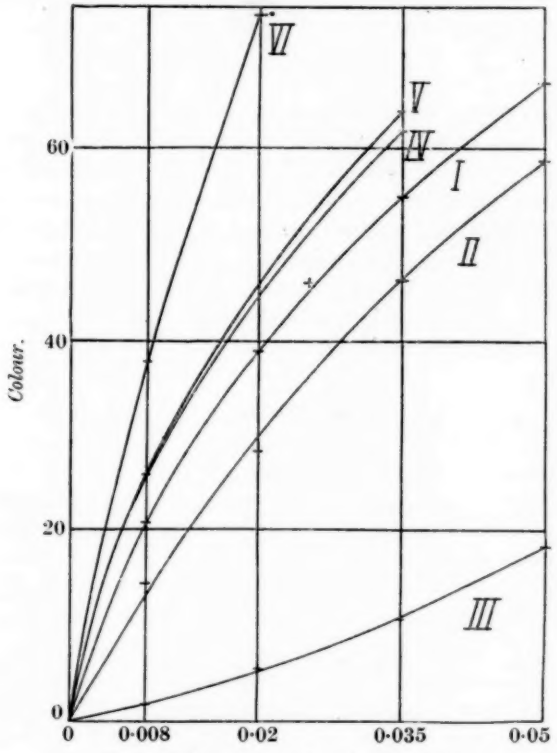
TABLE II.

Hydrated alum, gram per c.c.	Solution in	Colour.
0·050	Water	67
0·035	,,	55
0·025	,,	46
0·020	,,	39
0·008	,,	21
0·050	0·11 *N*-sulphuric acid	59
0·035	,,	46
0·020	,,	28
0·008	,,	15
0·100	0·108 *N*-sulphuric acid	46
0·050	,,	19*
0·035	,,	11*
0·020	,,	6*
0·008	,,	2*
0·035	0·1 *N*-ammonium sulphate	64
0·008	,,	26
0·035	1·0 *N*-ammonium sulphate	106
0·020	,,	74
0·008	,,	37
0·035	0·1 *N*-sucrose	62
0·008	,,	25
0·035	0·1 *N*-potassium chloride	62
0·008	,,	25
0·040	,,	69
0·040	0·3 *N* ,,	76
0·040	1·0 *N* ,,	95
0·040	3·0 *N* ,,	?
0·040	50 per cent. alcohol	135

The asterisk denotes an indirect determination.

The solution in 3·0*N*-potassium chloride was so altered in nature that it could not be matched against the glass plate or iron alum

solutions in water, whilst it matched quite easily against ferric chloride solution. Some of the results are shown graphically in the figure. It is clear that the addition of sulphuric acid lessens the colour (in a concentrated solution of sulphuric acid the colour is only a very faint greenish-brown, so that the non-hydrolysed salt



Concentration of iron alum in grams per c.c.

I. *Iron alum alone.*
II. ,, ,, *in presence of* 0·01 *N*-H_2SO_4.
III. ,, ,, ,, ,, ,, 0·11 *N*-H_2SO_4.
IV. ,, ,, ,, ,, ,, 0·1 *N-sucrose or* KCl.
V. ,, ,, ,, ,, ,, 0·1 $(NH_4)_2SO_4$.
VI. ,, ,, ,, ,, ,, 1·0 *N*-$(NH_4)_2SO_4$.

is probably only faintly coloured); the other substances all increase the colour, dilution and heating having the same effect.

The red colour of ferric salt solutions is often said to be due to the presence of colloidal ferric hydroxide (Ostwald, "Principles of Chemistry"); the evidence now recorded points to the colour of iron alum solution being due to the presence of a soluble basic

sulphate, which slowly changes to the insoluble form. If the colour were due to the hydroxide, it should be possible to match solutions of different iron salts against one another; but ferric chloride does not match with iron alum, and the latter will not match against an iron alum solution containing much potassium chloride, whilst the former will do so; this is easily explained if the iron alum colour is due to basic sulphate and the ferric chloride to basic chloride; the two basic salts are not of the same colour, and the addition of potassium chloride to iron alum causes the formation of basic chloride.

If the solution contains colloidal ferric hydroxide, the precipitate would be expected to have this composition instead of, as is the case, that of the basic sulphate, $2Fe_2O_3,SO_3$.

It is difficult to see why the addition of ammonium sulphate should produce such a large increase in the hydrolysis if the products are sulphuric acid and ferric hydroxide; one would expect that by the hydration of the added ammonium sulphate or its ions, water would be made virtually unavailable for hydrolysis, and so this would be decreased.

On the supposition that the colour is due to basic sulphate, the hydrolysis may be represented by the following equations:

$$2Fe_2(SO_4)_3 + 2(NH_4)_2SO_4 + 5H_2O \rightleftharpoons 2Fe_2O_3,SO_3 + 5H_2SO_4 + 2(NH_4)_2SO_4,$$

or

$$4Fe''' + 4NH'_4 + 8SO''_4 + 5H_2O \rightleftharpoons 2Fe_2O_3,SO_3 + 10H' + 4NH'_4 + 7SO''_4,$$

or

$$4Fe''' + SO''_4 + 5H_2O \rightleftharpoons 2Fe_2O_3,SO_3 + 10H'.$$

The Equilibrium Constant, $K = \frac{[Fe'''']^4 \times [SO''_4]}{[\text{basic salt}] \times [H']^{10}}$.—The addition of ammonium sulphate, by increasing the concentration of the SO_4 ions, will increase the hydrolysis; whilst the addition of sulphuric acid will, on the whole, produce the opposite effect, since the equilibrium equation shows that the effect of the hydrogen ions will more than counterbalance the effect of the SO_4 ions added at the same time. The increase of colour in the presence of dilute potassium chloride is probably due to the formation of basic chloride in addition to the basic sulphate already present.

Sucrose and alcohol increase the colour to some extent; the alcohol may conceivably do so by combining with the acid to form ethyl hydrogen sulphate, but why sucrose should affect the colour is not at all clear, unless it too combines with the acid.

Colour Change with Time.—All the measurements referred to

above were made as soon as possible after the preparation of the solutions.

When a dilute solution was allowed to remain it was noticed that the colour apparently changed with time. A series of measurements was therefore made on a 1 per cent. solution of alum in water, with the following results, calling the colour of a fresh solution 100:

Time in hours ...	0	1	3	5	24	29	124
Colour.....	100	109	136	130	115	111	98

Similar results were obtained with a 5 per cent. solution, but the change was slower. The fact that the colour rises to a maximum and then decreases might be due to the process of hydrolysis occupying an appreciable time, the decrease being due to precipitation occurring.

It is thought more likely, however, that the increase in colour is only apparent, and not real; the solution after one hour showed a distinctly perceptible cloudiness, due to suspended, finely divided solid; this would have the effect of obscuring some of the light, so that in the colorimeter the solution would appear darker than it really was; it is noticeable that it is difficult to obtain a good match between a fresh solution and an older one, and this is explainable in the same way. A perceptible deposit appears on the bottom of the bottle after the maximum colour is reached, so that the decrease of colour which follows is due to the gradual deposition of the basic sulphate to which the colour is due. If the change of colour were due to progressive hydrolysis, a corresponding change in the electrical conductivity would be expected; with the 1 per cent. solution the conductivity variations were less than 0·3 per cent. during eight days, at the end of which time there was a considerable precipitate present.

In connexion with this work, a number of density determinations of aqueous iron alum solutions have been made, and since these do not appear to have been previously recorded, they are given below. The determinations were made in 50 c.c. Gay-Lussac specific gravity bottles fitted with a ground-on cap covering the stopper and the neck of the bottle. A 100 litre, gas-heated thermostat was used, temperature variations being less than 0·01°. All weighings were corrected to a vacuum separately, and the densities are considered to be correct to the fifth place.

Densities and Apparent Molecular Solution Volume of Anhydrous Iron Ammonium Alum Solutions at 32·5°.

Weight of hydrated alum per c.c.	Density.	Apparent molecular solution volume.
0·2000	1·0796	124·3
0·1500	1·05907	120·1
0·1000	1·03801	116·8
0·0502	1·01670	113·7
0·0350	1·01025	109·6
0·0250	1·00592	107·4
0·0201	1·00376	105·0
0·0080	0·99849	99

Summary.

1. The hydrolysis of ferric ammonium alum has been investigated.

2. The precipitate, which separates on keeping, is found to have the composition $2Fe_2O_3,SO_3$.

3. The colour of iron alum solutions alone and in the presence of other substances has been measured, and is shown to be in agreement with the supposition that the colour is due to the presence of a soluble form of the basic sulphate of the composition shown above.

4. A white precipitate obtained on adding concentrated sulphuric acid is found to be the anhydrous alum.

5. The densities of some aqueous iron alum solutions are recorded.

CEYLON MEDICAL COLLEGE. [*Received, November 7th,* 1916.]

C.—*Additive Compounds of Trinitrobenzene*

By JOHN JOSEPH SUDBOROUGH.

IN continuation of the investigations on the capacity of polynitro-aromatic compounds to form additive derivatives (compare T., 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773; 1911, **99**, 209) the compounds enumerated in tables I—IV have been prepared.

During the progress of this work descriptions of a few additive compounds of aromatic hydrocarbons with polynitro-compounds have appeared. Kremann (*Monatsh.*, 1911, **32**, 609) has described a compound of trinitrobenzene with fluorene in the molecular proportions of 3 to 2, and A. Buguet (*Compt. rend.*, 1909, **149**, 857) has prepared compounds of *s*-trinitrobenzene with phenanthrene

and acenaphthene, the compounds consisting of equimolecular quantities of the components.

The compounds characterised by an asterisk could only be obtained by using an excess of the hydrocarbon or base. In all the other cases the products were prepared by using theoretical quantities of trinitrobenzene and of hydrocarbon or base and crystallising from a suitable solvent, usually alcohol, but occasionally benzene. In the case of *p*-aminobenzophenone a mixture of benzene with a little alcohol was used, and with the diethylphenylenediamines, a mixture of benzene and light petroleum.

Conclusions.

(1) One of the most interesting facts established is that aromatic hydrocarbons form additive compounds with trinitrobenzene in much the same manner that they do with picric acid. Many of these compounds are comparatively stable, and can be crystallised from suitable solvents. As a rule the colour of these additive compounds is not so marked as the colours of the corresponding amino- or hydroxy-derivatives. It will be noticed that the colour of the hydrocarbon additive compounds is usually yellow, with the exception of the compound with anthracene, the colour of which is bright red.

In a previous communication (T., 1910, **97**, 780) it was suggested that the formation of additive compounds from aromatic amines, phenols, phenolic ethers, and sulphur compounds could probably be attributed to the latent valencies of the nitrogen, oxygen, or sulphur atoms. The isolation of stable compounds of hydrocarbons with trinitrobenzene raises the question as to whether in all cases the addition may not be of the same type and be due to the unsaturated character of the aromatic nucleus present.

It is hoped that a study of the ultraviolet absorption spectra of some of these compounds may throw some light on this question.

It is well known that quinones form coloured additive compounds with phenols and aromatic amines, and Pfeiffer has shown recently (*Annalen*, 1914, **404**, 1) that phenolic ethers and aromatic hydrocarbons, such as durene and hexamethylbenzene, also form coloured additive compounds with chloranil. From this Pfeiffer concludes that the addition is not due to the presence of the amino-, substituted amino-, or hydroxy-group present in the amine or phenol, but is due to the unsaturated aromatic nucleus, each carbonyl group being able to satisfy the latent valencies of one benzene nucleus, and he represents such additive compounds by the following type of formula:

$$C_6Me_6 \ldots O{:}C_6H_4{:}O \ldots C_6Me_6.$$

It would appear probable that the formation of compounds between polynitro-aromatic compounds on the one hand and aromatic hydrocarbons, amines, phenols, phenolic ethers, and sulphur compounds on the other is due to latent valencies of the nitro-groups and of the aromatic residues of the hydrocarbon, phenol, or amine (compare Pfeiffer, *loc. cit.*, p. 13). The hydroxy-, alkyloxy-, amino-, and alkylamino-groups act mainly as auxochromes, but at the same time tend to increase the stability of the additive compounds.

On Pfeiffer's scheme these additive compounds are represented as follows:

$$C_6H_3(NO_2)_3 \ldots C_{10}H_8.$$
$$C_6H_3(NO_2)_3 \ldots C_{10}H_7{\cdot}OH.$$
$$C_6H_3(NO_2)_3 \ldots C_{10}H_7{\cdot}NH_2.$$

(2) The question of the number of molecules of trinitrobenzene with which one molecule of the aromatic compound can combine is of considerable importance. An examination of the various additive compounds prepared by Somerhoff (*Diss.*, Zurich, 1904) and the present author tends to prove that the number of molecules of trinitrobenzene does not vary with the number of amino-, substituted amino-, hydroxy-, or alkyloxy-groups present, but rather with the number of aromatic nuclei. In this connexion a condensed system of several benzene or of benzene and heterocyclic rings has to be regarded as a single nucleus.

The following substances form additive compounds of the type one molecule of trinitrobenzene with one molecule of the substance: The hydrocarbons naphthalene, anthracene, phenanthrene, acenaphthene, chrysene, and retene; aniline, its homologues and substituted derivatives; mono- and di-alkylated anilines; naphthylamines, their alkyl derivatives and substitution products; naphthols and alkylated naphthols; phenylenediamines, tolylenediamines, and naphthylenediamines; triaminotoluene; phenylhydrazones derived from aliphatic ketones; quinoline, *iso*quinoline, their tetrahydro-derivatives, and substituted amino- and hydroxy-derivatives; methylindole, phenylpyrazolones.

The following groups of substances form additive compounds of the type two molecules of trinitrobenzene with one molecule of the substance: Hydrocarbons containing two benzene nuclei, for example, *s*-diphenylethane, stilbene, tolane, dihydroanthracene, α-dinaphthylmethane, and their amino-derivatives, for example, diaminostilbene, aminodiphenylmethane, and diaminodiphenylmethane. Aromatic secondary amines, for example, diphenylamine, phenyl-α- and -β-naphthylamines, αα- and ββ-dinaphthylamines, various tolylnaphthylamines. Derivatives of aromatic

ketones, for example, tetramethyldiaminobenzophenone. Phenylhydrazones derived from aromatic aldehydes or ketones, for example, benzaldehydephenylhydrazone, cinnamaldehydephenylhydrazone, acetophenonephenylhydrazone. Esters containing two or more benzene nuclei, for example, benzyl salicylate, quinol disalicylate. Benzylidene compounds containing two aromatic nuclei, for example, distyryl diketone; benzylidene β-naphthylamine. Phenolic ethers containing two aromatic nuclei, for example, phenylnaphthyl ethers and dinaphthyl ethers. Azo-compounds, for example, dimethylaminoazobenzene, aminoazonaphthalene. Certain sulphur compounds containing two benzene nuclei, dimethylaniline disulphide, *o*-diaminodiphenyl disulphide, 1-phenylbenzothiazole,

$$C_6H_4\!<\!\overset{N}{S}\!>\!CPh.$$

There are, however, various exceptions to these generalisations:

(*a*) Several compounds form additive compounds of two different types. Thus phenyl-β-naphthylamine, asarone (trimethoxypropenylbenzene), and tetramethyldiaminobenzophenone can give compounds containing equimolecular quantities of the components and also compounds containing two molecules of trinitrobenzene to one of amine. Both series of compounds are stable.

(*b*) Quite a number of substances containing two or more independent aromatic nuclei form compounds with trinitrobenzene in the molecular proportions one to one. Among such substances may be mentioned: 1-benzeneazo-2-naphthylamine, diethylaminobenzylidene-*p*-aminomethylaniline, *o*:*o*-diaminostilbene, tetramethyl-*p*-diaminotriphenylmethane, tetramethyldiaminobenzhydrol, tetramethyldiaminotriphenylmethane, paraleucaniline, aminobenzophenone, phenyl salicylate, phenyl-α-naphthyl ether, benzylidene-α-naphthylamine, *m*-nitrobenzaldehydephenylhydrazone, αα-diphenylpyridine, acridine and its derivatives, triphenylpyrrole.

(*c*) In a few cases one molecule of trinitrobenzene combines with two molecules of the substances, for example, carbostyril, dibenzylaniline, and naphthionic acid. The additive compound of trinitrobenzene and fluorene has the molecular ratio 3:2.

(4) The auxochrome effect of amino- and hydroxy-groups is well observed in the case of quinoline and its derivatives. Quinoline itself gives an additive compound which is almost colourless, whereas the hydroxyquinolines give yellow or brown additive compounds and the aminoquinolines give stable, red, crystalline compounds. The auxochrome effect of an ethylene linking is also observed in the case of stilbene. Thus *s*-diphenylethane gives a very pale yellow-coloured additive compound, and the unsaturated analogue

stilbene a deep canary-coloured compound. Tolane also yields a deep yellow-coloured product.

The difference in colour between the additive compounds of trinitrobenzene with anthracene and dihydroanthracene is also marked.

(5) The results show that most naphthalene derivatives form additive compounds with trinitrobenzene, and that the colour of such compounds is yellow unless an auxochrome such as an amino-, a substanced amino-group, or several hydroxyl groups are present. Substituents such as Br, NO_2, CN, CO_2Et, CHO, Bz do not interfere with the formation of additive compounds. Naphthalene derivatives containing the $SO_2{\cdot}OH$ or SO_2Cl groups, on the other hand, do not appear to form additive compounds with trinitrobenzene.

(6) Pyrrole, its phenyl, tolyl, and triphenyl derivatives all yield additive compounds with trinitrobenzene. The compound with pyrrole has a yellow colour (van Romburgh, *Rec. trav. chim.*, 1895, **14**, 67), those with phenyl- and tolyl-pyrroles a canary yellow colour, and the compound with triphenylpyrrole a purple colour.

(7) Attention has already been drawn (T., 1910, **97**, 776) to the difference in colour between the additive compounds of benzene with quinoline derivatives on the one hand and with tetrahydro-derivatives of quinoline on the other. Another example is given here, namely, 1-ethyltetrahydroquinoline, which forms a black additive compound with trinitrobenzene.

(8) So far it has not been found possible to isolate additive compounds of trinitrobenzene with the following substances: Diphenylmethane, triphenylcarbinol, diphenylfulvene, xanthone, fluorenone, benzil, cinnamylideneacetic acid, resorcinol dimethyl ether, *p*-dihydroxydiphenylmethane, *pp*-diphenol, naphthalenesulphonic acids and- sulphonyl chlorides, acetyl-*p*-phenylenediamine, benzamidine, piperazine, antipyrine, phenacetin, strychnine, bornylamine.

In conclusion, I have to thank Messrs. S. H. Beard and R. Rungaswamy Naidu for valuable assistance in the analytical portion of the work.

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Bangalore. [*Received, August 15th*, 1916.]

TABLE I.

Additive Compounds of Aromatic Hydrocarbons with s-*Trinitrobenzene.*

Component.	Mols. of nitro-compound to mols. of hydrocarbon.	Formula.	Appearance.	M. p.	Analysis. Found per cent.	Analysis. Calculated per cent.
S-Diphenylethane	2 : 1	$C_{26}H_{20}O_{12}N_6$	Pale yellow crystals	102°	N=13·80	13·81
Stilbene	2 : 1	$C_{26}H_{18}O_{12}N_6$	Well developed, canary crystals	120	N=13·91	13·86
Tolane	2 : 1	$C_{26}H_{16}O_{12}N_6$	Lustrous deep yellow, quadratic slates	96	N=13·97	13·91
Naphthalene	1 : 1	$C_{16}H_{11}O_6N_3$	Pale yellow needles	152·5	N=12·31	12·32
β-Methylnaphthalene	1 : 1	$C_{17}H_{13}O_6N_3$	Canary yellow needles	123	N=11·9	11·83
Anthracene	1 : 1	$C_{20}H_{13}O_6N_3$	Scarlet needles	164	N=10·92	10·74
Dihydroanthracene	2 : 1	$C_{26}H_{18}O_{12}N_6$	Yellow needles	92—92·5	N=13·8	13·86
Dibromoanthracene	1 : 1	$C_{20}H_{11}O_6N_3Br_2$	Feathery red needles	179	Br=28·8	29·1
Phenanthrene	1 : 1	$C_{20}H_{13}O_6N_3$	Glistening orange needles or plates	158	N=10·84	10·74
Fluorene	3 : 2	$C_{44}H_{29}O_{18}N_9$	Golden-yellow plates	—	N=13·1	13·0
Acenaphthene	1 : 1	$C_{18}H_{13}O_6N_3$	Golden-yellow needles	168	N=11·9	11·4
Acenaphthylene	1 : 1	$C_{18}H_{11}O_6N_3$	Golden-yellow needles	221	N=12·0	11·5
Chrysene	1 : 1	$C_{24}H_{15}O_6N_3$	Canary-yellow needles	186	N= 9·62	9·52
Retene	1 : 1	$C_{24}H_{21}O_6N_3$	Yellow needles	139—140	N= 9·45	9·40
α-Dinaphthylmethane	2 : 1	$C_{33}H_{22}O_{12}N_6$	Bright yellow, glistening plates	141·5	N=12·24	12·10

TABLE II.

Additive Compounds of Naphthalene Derivatives with s-Trinitrobenzene.

Component.	Mols. of trinitro-benzene to Mols. of naptha-lene derivative.	Formula.	Appearance.	M. p.	Analysis. Found per cent.	Analysis. Calculated per cent.
α-Bromonaphthalene	1 : 1	$C_{16}H_{10}O_6N_3Br$	Lemon-yellow needles	137°	N=10·15	10·00
α-Dibromonaphthalene	1 : 1	$C_{16}H_9O_6N_3Br_2$	Lemon-yellow needles	123	Br=32·0	32·1
α-Nitronaphthalene	1 : 1	$C_{16}H_{10}O_8N_4$	Pale yellow, prismatic needles	72—73	N=14·45	14·51
*α-Naphthonitrile	1 : 1	$C_{17}H_{10}O_6N_4$	Pale yellow crystals	88	N=15·26	15·30
β-Naphthonitrile	1 : 1	$C_{17}H_{10}O_6N_4$	Pale yellow crystals	95	N=15·35	15·30
*α-Naphthoic acid	1 : 2	$C_{28}H_{19}O_{10}N_3$	Pale yellow needles	182·5	N= 7·7	7·6
Methyl α-naphthoate.....	1 : 1	$C_{18}H_{13}O_8N_3$	Pale yellow needles	107	N=10·56	10·53
Methyl β-naphthoate	1 : 1	$C_{18}H_{13}O_8N_3$	Pale yellow needles	104·5	N=10·54	10·53
α-Naphthyl methyl ketone	1 : 1	$C_{18}H_{13}O_7N_3$	Sulphur-yellow needles	112	N=11·0	11·0
Phenyl α-naphthyl ketone	1 : 1	$C_{23}H_{15}O_7N_3$	Pale yellow needles	89	N= 9·38	9·43
β-Naphtholaldehyde	1 : 1	$C_{17}H_{11}O_8N_3$	Feathery-brown needles	137	N=10·77	10·91
α-Naphtholphthalein	1 : 1	$C_{34}H_{21}O_{10}N_3$	Well developed brownish-yellow crystals	235	N= 6·7	6·66
1 : 3-Dihydroxynaphthalene	1 : 1	$C_{16}H_{11}O_8N_3$	Brick-red needles	174·5	N=11·11	11·26
Ethyl naphthylcarbamate	1 : 1	$C_{19}H_{16}O_8N_4$	Canary-yellow needles	91·5—92	N=13·08	13·08
*αα-Azonaphthalene	2 : 1	$C_{32}H_{20}O_{12}N_8$	Russet-brown needles	198	N=16·41	15·82
α-Aminoazonaphthylene	2 : 1	$C_{32}H_{22}O_{12}N_9$	Brilliant black needles	232—233	N=17·2	17·40
4-Amino-l-naphthyl ethyl ether	1 : 1	$C_{18}H_{16}O_7N_4$	Glistening purplish-black needles	177·5	N=14·0	14·47
4-Acetylamino-l-naphthyl ethyl ether	1 : 1	$C_{20}H_{18}O_8N_4$	Bright red needles	156·5	N=12·7	12·9

Table III.

Additive Compounds of s-Trinitrobenzene with Cyclic Bases and with some Benzene Derivatives.

A.—Benzene derivatives.	Mols. of nitro-compound to Mols. of amine.	Formula.	Appearance.	M. p.	Analysis. Found per cent.	Analysis. Calculated per cent.
**p*-Aminobenzophenone	1 : 1	$C_{19}H_{14}O_7N_4$	Dark yellowish-brown prisms	*11°	N=13·85	13·66
*Dibenzylaniline	1 : 2	$C_{46}H_{41}O_6N_5$	Dark ruby-red prisms	86—87	N= 9·5	9·2
Ethyl 3 : 5-diaminobenzoate ...	1 : 1	$C_{15}H_{15}O_8N_5$	Bright brick-red plates	139	N=18·2	17·8
*Diethyl-*m*-phenylenediamine ...	—	—	Prune-coloured prisms	88·5	—	—
*Diethyl-*p*-phenylenediamine	1 : 1	$C_{16}H_{19}O_6N_5$	Bluish-black needles	79	N=19·0	18·6
o-Dianisidine	2 : 1	$C_{26}H_{22}O_{14}N_8$	Flat black needles	144	N=16·6	16·7
3 : 5-Diaminoanisole	1 : 1	$C_{13}H_{13}O_7N_5$	Dark reddish-brown needles	130	N=20·0	19·9
p-Aminodiphenylamine	2 : 1	$C_{24}H_{18}O_{12}N_8$	Black plates	105·5	N=18·5	18·5
Aminodiphenylmethane	2 : 1	$C_{25}H_{29}O_{12}N_7$	Brick-red prisms	66—67	N=16·4	16·1
Diaminodiphenylmethane.....	2 : 1	$C_{25}H_{20}O_{12}N_8$	Dark brown, flat prisms	132·5	N=18·2	18·0
Paraleucaniline	1 : 1	$C_{25}H_{22}O_6N_6$	Prune-black prisms	140	N=16·8	16·7
Dimethylaminoazobenzene	2 : 1	$C_{26}H_{21}O_{12}N_9$	Reddish-black plates	135·5	N=19·7	19·4
2 : 4-Bisbenzeneazophenol	2 : 1	$C_{30}H_{20}O_{13}N_{10}$	Golden-brown plates	125	N=19·0	19·2
2-Amino-1-naphthyl ethyl ether	1 : 1	$C_{18}H_{16}O_7N_4$	Purplish-black needles	177·5	N=14·5	14·0
Ethyl phloroglucinoldicarboxylate	1 : 1	$C_{16}H_{17}O_{13}N_3$	Pale yellow needles	76	N= 8·8	8·7
Distyryl diketone	2 : 1	$C_{29}H_{20}O_{10}N_6$	Sulphur-yellow needles	125	N=12·65	12·7
Phenyl cinnamylidenemethyl ketone	1 : 1	$C_{22}H_{17}O_7N_3$	Lemon-yellow plates	108	N=10·1	9·4
Piperine	1 : 1	$C_{23}H_{22}O_9N_4$	Scarlet, prismatic needles	130	N=11·3	11·2
Ethyl piperate	—	—	Orange-red needles	90—91	—	—

TABLE III.

Additive Compounds of s*-Trinitrobenzene with Cyclic Bases and with some Benzene Derivatives* (continued).

B.—Cyclic Nitrogen Compounds.	Mols. of nitro-compound to Mols of amine.	Formula.	Appearance.	M. p.	Analysis. Found per cent.	Analysis. Calculated per cent.
4-Aminoquinoline	1 : 1	$C_{15}H_{11}O_6N_5$	Ruby-red prisms	111°	N=19·7	19·6
2-Aminoquinoline	1 : 1	$C_{15}H_{11}O_6N_5$	Bright crimson needles	186	N=19·9	19·6
Carbostyril	1 : 2	$C_{24}H_{17}O_8N_5$	Sulphur-yellow needles	178	N=13·8	13·9
1-Ethyltetrahydroquinoline	1 : 1	$C_{17}H_{18}O_6N_4$	Black needles	70—71	N=16·0	15·0
*Phenylpyrrole	1 : 1	$C_{16}H_{12}O_6N_4$	Canary-yellow needles	80	N=15·96	15·73
*Tolylpyrrole	1 : 1	$C_{17}H_{14}O_6N_4$	Canary-yellow plates	77	N=15·26	15·14
Triphenylpyrrole	1 : 1	$C_{28}H_{20}O_6N_4$	Purple needles	136·5—137	N=11·27	11·02
Methylacridine	1 : 1	$C_{20}H_{14}O_6N_4$	Greenish-yellow needles	120—120·5	N=13·8	13·8
Phenylacridine	1 : 1	$C_{25}H_{16}O_6N_4$	Dark ruby-red prisms	139·5	N=12·0	12·0
Diphenylpiperazine	2 : 1	$C_{28}H_{24}O_{12}N_8$	Ruby-red plates	171	N=16·9	16·9
3-Aminocarbazole	1 : 1	$C_{18}H_{13}O_6N_5$	Purplish-black plates	195	N=17·35	17·7
3-Acetylaminocarbazole	1 : 1	$C_{20}H_{15}O_7N_5$	Dark red needles	193·5	N=16·15	16·02
3 : 5-Diphenylpyrazole	2 : 1	$C_{27}H_{18}O_{12}N_8$	Sulphur-yellow prisms	135·5	N=17·6	17·3
Aminostrychnine	2 : 1	$C_{33}H_{29}O_{14}N_9$	Red needles	161	N=16·45	16·3

TABLE IV.

Additive Compounds of some Aromatic Sulphur Compounds with s-*Trinitrobenzene.*

Components.	Mols. of nitro-compound to mols. of sulphur compound.	Formula.	Appearance.	M. p.	Analysis. Found per cent.	Analysis. Calculate per cent.
Thionaphthol	1 : 1	$C_{16}H_{11}O_6N_3S$	Bright yellow needles	15°	N = 11·47	11·26
Dithioresorcinol	1 : 1	$C_{12}H_8O_6N_2S_2$	Bright yellow crystals	76—77	S = 18·02	18·03
1-Phenylbenzthiazole	2 : 1	$C_{25}H_{15}O_{12}N_7S$	Glistening yellow needles	106	N = 15·49	15·38
Dimethylaniline disulphide	2 : 1	$C_{28}H_{26}O_{12}N_8S_2$	Deep prune-coloured needles	97·5	N = 15·50	15·33
o-Diaminodiphenyl disulphide .	2 : 1	$C_{24}H_{18}O_{12}N_8S_2$	Dark brick-red needles	100	N = 16·71	16·62
Thiodiphenylamine	1 : 1	$C_{18}H_{13}O_6N_4S$	Black needles	124·5	S = 7·46	7·77

CI.—*Additive Compounds of* s-*Trinitrobenzene with Amino-derivatives of Complex Aromatic Hydrocarbons.*

By Shunker Trimbak Cadre and John Joseph Sudborough.

In a series of papers it has been pointed out that *s*-trinitrobenzene forms additive compounds with many aromatic hydrocarbons, amines, phenols, and phenolic ethers (T., 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583; 1910, **97**, 773; 1911, **99**, 209; this vol., p. 368). As a rule the additive compounds obtained from naphthalene derivatives are more stable than those derived from the corresponding benzene compounds, and the object of the work described in this paper has been to ascertain whether the amino-derivatives of complex hydrocarbons, such as phenanthrene, anthracene, acenaphthene, and fluorene, yield still more stable additive compounds with trinitrobenzene.

The behaviour of trinitrobenzene towards the following compounds has been studied: α- and β-modifications of 9-aminophenanthrene, 4-aminophenanthrene and the isomeric 2-amino-compound, 9-aminoanthracene, α- and β-anthramines, α- and β-anthrols, their ethyl ethers and the potassium derivative of α-anthrol, 2-aminofluorene, diaminofluorene, and 9-aminoacenaphthene.

The experiments prove that all the amino-derivatives examined yield additive compounds with trinitrobenzene. With the exception of aminofluorene, all the compounds are formed by the union of equimolecular quantities of the base and of trinitrobenzene.

The colours of the additive compounds are relatively deep, being, as a rule, either black or deep brown.

The additive compounds derived from anthracene are relatively more deeply coloured than those derived from naphthalene, as shown in the following table:

	Colour of additive compounds.		Colour of additive compounds.
Anthracene...	Scarlet	Naphthalene.....	Pale yellow
α-Anthramine	Black	α-Naphthylamine	Brick-red
β- „	„	β- „	„
α-Anthrol ...	Deep reddish-brown	α-Naphthol	Orange-yellow
β- „ ...	„	β- „	„
Ethyl ethers..	Scarlet or brick-red	Ethyl ethers	Canary-yellow

The compounds are comparatively stable, and can be crystallised from most solvents, but determinations of the molecular weights show that in dilute benzene solution nearly complete dissociation into the components takes place.

The compounds, on the whole, resemble the additive compounds from the naphthylamines, but several of them appear to be incapable of yielding acetyl derivatives.

The additive compounds derived from α- and β-anthrols and their ethyl ethers are not so deeply coloured as the corresponding compounds from α- and β-anthramine. This is in complete accord with previous results, and is to be attributed to the feebler auxochrome effect of the hydroxyl group as compared with the amino-group (compare this vol., p. 369, also T., 1911, **99**, 209).

Experimental.

α-9-*Aminophenanthrene.*—The additive compound,

$$C_{14}H_9\cdot NH_2,C_6H_3(NO_2)_3,$$

separates when hot alcoholic solutions of its components are mixed; it crystallises from chloroform in dark, chocolate-coloured needles melting at 220—221°:

0·2863 gave 40·6 c.c. N_2 at 27° and 671 mm. N = 14·0.
$C_{20}H_{14}O_6N_4$ requires N = 13·8 per cent.

0·1130, dissolved in 17·42 benzene, lowered the freezing point 0·149°. M.W. = 218.

0·202, in 13·065 benzene, raised the boiling point 0·187°. M.W. = 221. The completely dissociated compound requires M.W. = 203.

When warmed with acetic anhydride the additive compound yields an *acetyl* derivative, $C_{14}H_9\cdot NH\cdot CO\cdot CH_3,C_6H_3(NO_2)_3$, which crystallises from 90 per cent. alcohol in golden-yellow needles melting at 190°:

0·0880 gave 11·0 c.c. N_2 at 23° and 686 mm. N = 12·8.
$C_{22}H_{16}O_7N_4$ requires N = 12·5 per cent.

The β-modification of 9-aminophenanthrene also forms an *additive* compound, $C_{20}H_{14}O_6N_4$, with *s*-trinitrobenzene. This crystallises from alcohol in pale red, nodular masses, or from chloroform, in which it is readily soluble, in clusters of minute, red crystals melting at 104·5—105°:

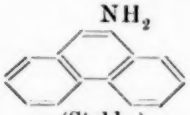
0·1387 gave 18·3 N_2 at 25° and 689 mm. N = 13·5.

It is partly decomposed into its components when crystallised from alcohol, and is characterised by its pale colour as compared with the additive compounds of other aromatic amino-derivatives. It differs also from almost all the other additive compounds derived from primary amines in that it does not appear to be decomposed by hydrogen chloride.

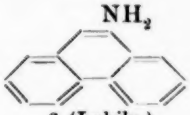
A convenient method of estimating the percentage of *s*-trinitrobenzene in many of these additive compounds is to decompose them

with dilute hydrochloric acid and weigh the trinitrobenzene left after washing with water. This method works well provided the hydrochloride of the base is fairly readily soluble in water. When the hydrochloride of the base is sparingly soluble in water, or is readily hydrolysed by water, a convenient method is to dissolve the additive compound in benzene, pass in dry hydrogen chloride, then remove the precipitated hydrochloride, wash with benzene, and after removal of the benzene weigh the trinitrobenzene. This method gave good results with the additive compounds from α-9-aminophenanthrene and aminofluorene, but the additive compound derived from β-9-aminophenanthrene is not decomposed when hydrogen chloride is passed into its benzene solution.

Schmidt and Heinle (*Ber.*, 1911, **44**, 1493) have suggested the following formulæ for the α- and β-modifications of 9-aminophenanthrene:

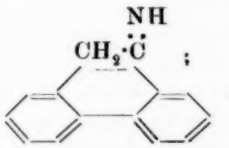


α (Stable.)



β (Labile.)

The pale colour of the additive compound derived from the β-modification and the fact that the compound does not appear to be decomposed by hydrogen chloride points rather to the absence of an amino-group in the original base. It is possible that the base has an imino-group, and may perhaps be represented by the formula:



4-*Aminophenanthrene*.—The additive compound,

$$C_{14}H_9{\cdot}NH_2,C_6H_3(NO_2)_3,$$

crystallises from alcohol in chocolate, prismatic needles with shining faces, melting at 195—196°:

0·1601 gave 22·5 c.c. N_2 at 27° and 673 mm. N = 14·0.

$C_{20}H_{14}O_6N_4$ requires N = 13·8 per cent.

It yields a pale yellow *acetyl* derivative.

2-*Aminophenanthrene*.—The additive compound crystallises from alcohol in slender, prismatic needles melting at 175—176°. The amount obtained was too small for analysis.

2-*Aminofluorene*.—When molecular quantities of the base and trinitrobenzene are separately dissolved in alcohol and the two solutions mixed, a dark-coloured additive compound separates,

together with a little trinitrobenzene. The additive compound crystallises from alcohol in reddish-chocolate-coloured needles melting at 116—117°:

0·1447 gave 0·3190 CO_2 and 0·0508 H_2O. C = 60·10; H = 3·90.
0·1365 „ 18·2 c.c. N_2 at 22° and 684 mm. N = 13·7.
0·3356 „ 0·1622 trinitrobenzene (m. p. 121°) = 48·3.

These results agree best with the formula

$$5C_{13}H_9{\cdot}NH_2,4C_6H_3(NO_2)_3,$$

as shown by the following table:

Ratio of Mols. of Base to Trinitrobenzene.

	1 : 1	3 : 2	5 : 4	Found.
C	57·9	63·2	60·7	60·1
H	3·55	4·02	3·8	3·9
N	14·8	13·0	13·5	13·7
Trinitrobenzene	54·1	44·0	48·5	48·3

The composition of this compound is more complex than that of any of the additive compounds hitherto studied. Fluorene itself (this vol., p. 369) yields a compound, $3C_6H_3(NO_2)_3,2C_{13}H_{10}$, but most hydrocarbons, amines, and phenols yield compounds of the type 1 mol. of trinitrobenzene and 1 mol. of the substance, or 2 mols. of trinitrobenzene and 1 mol. of the substance.

Confirmation of the above composition was obtained by taking the base and trinitrobenzene in different proportions, mixing their alcoholic solutions, and determining whether pure additive compound or additive compound with excess of trinitrobenzene or base separated. It was found that when the two components were employed in the molecular proportions 5 : 4 nothing but additive compound could be isolated. When other proportions were used small amounts of colourless crystals were obtained in some of the later fractions, and these could usually be identified as trinitrobenzene or aminofluorene.

Determination of the molecular weight by the cryoscopic method in benzene solution gave the following results:

i. 0·1390 in 17·42 benzene gave $\Delta t = -$ 0·2103° M.W. = 190.
ii. 0·1691 in 17·42 „ „ 0·2686° M.W. = 181.

When the additive compound was prepared from benzene solutions dark, chocolate-brown needles melting at 114—115° were obtained. On analysis these proved to have the composition $C_{13}H_9{\cdot}NH_2,C_6H_3(NO_2)_3$:

0·1458 gave 20·6 c.c. N_2 at 29° and 689 mm. N = 14·2.
0·1032 „ 0·0550 trinitrobenzene (m. p. 121°) = 53·3.

$C_{19}H_{14}O_6N_4$ requires N = 14·2; trinitrobenzene = 54·1 per cent.

The compound obtained from benzene solution when acetylated with acetic anhydride gave an *acetyl* derivative, which crystallised from benzene in orange-coloured needles melting at 180—181°:

0·0738 gave 9·8 c.c. N_2 at 26° and 687 mm. N = 13·5.

A compound with the molecular ratio 5 : 4 requires N = 13·5 per cent.

Diaminofluorene.—A small amount of an *additive* compound was obtained from alcoholic solution in black-coloured needles melting at 210°.

9-*Aminoacenaphthene.*—This base combines with trinitrobenzene, and the product crystallises from alcohol or chloroform in dark, prune-coloured needles melting at 213—214°:

0·1326 gave 19·3 c.c. N_2 at 27° and 688 mm. N = 14·7.
0·1012 „ 0·0554 trinitrobenzene = 54·7.
$C_{18}H_{14}O_6N_4$ requires N = 14·7; trinitrobenzene = 55·7 per cent.

A determination of its molecular weight in benzene solution by the cryoscopic method proved that considerable dissociation into its components had occurred:

0·0515, in 17·42 benzene, gave $\Delta t = -0·069°$. M.W. = 214.
$C_{18}H_{14}O_6N_4$ requires M.W. = 382 per cent.

When acetylated the additive compound yields an *acetyl* derivative, which crystallises from alcohol in yellow needles melting at 157—158°.

9-*Aminoanthracene.*—The *additive* compound,

$$C_{14}H_{19}\cdot NH_2,C_6H_3(NO_2)_3,$$

prepared by mixing together hot alcoholic solutions of the components, crystallises from chloroform in minute, purplish-black needles melting at 215·5°:

0·1558 gave 20·45 c.c. N_2 at 18° and 689 mm. N = 13·8.
0·0928 „ 0·0488 trinitrobenzene (m. p. 121°) = 52·6.
$C_{20}H_{14}O_6N_4$ requires N = 13·8; trinitrobenzene = 52·4 per cent.

9-Acetylaminoanthracene does not appear to yield an additive compound with trinitrobenzene.

α-*Anthramine.*—The *additive* compound, $C_{20}H_{14}O_6N_4$, crystallises from alcohol in raven-black, slender needles melting at 206—207°:

0·1415 gave 19·0 c.c. N_2 at 21° and 690 mm. N = 14·0.
$C_{20}H_{14}O_6N_4$ requires N = 13·8 per cent.

α-Acetylanthramine does not form an additive compound with trinitrobenzene.

β-*Anthramine.*—β-Anthramine prepared from β-anthrol (*Annalen*, 1882, **212**, 57) yields an *additive* compound,

$$C_{14}H_9\cdot NH_2,C_6H_3(NO_2)_3,$$

which crystallises from alcohol in glistening, black needles melting at 168·5—169°:

0·0938 gave 12·8 c.c. N_2 at 22° and 693 mm. N = 14·2.

An additive compound could not be obtained from α-acetylanthramine and trinitrobenzene.

α-Anthrol.—α-Anthrol yields an *additive* compound,

$$C_{14}H_9{\cdot}OH,C_6H_3(NO_2)_3,$$

which crystallises from benzene in minute, dark, reddish-brown plates melting and decomposing at about 161°:

0·1024 gave 10·7 c.c. N_2 at 22° and 686 mm. N = 10·7.

$C_{20}H_{13}O_7N_3$ requires N = 10·3 per cent.

α-Anthrol Ethyl Ether.—The *additive* compound,

$$C_{14}H_9{\cdot}OEt,C_6H_3(NO_2)_3,$$

crystallises from alcohol or acetone in scarlet needles melting at 149·5—150·5°:

0·1173 gave 11·4 c.c. N_2 at 24° and 688 mm. N = 9·9.

$C_{22}H_{17}O_7N_3$ requires N = 9·7 per cent.

Potassium salt of α-Anthrol.—The *additive* compound,

$$C_{14}H_9{\cdot}OK,2C_6H_3(NO_2)_3,$$

crystallises from alcohol in black needles which are not molten at 275°:

0·1328 gave 0·0079 K. K = 5·9.

$C_{26}H_{15}O_{13}N_6K$ requires K = 5·9 per cent.

β-Anthrol forms an *additive* compound, also containing equimolecular proportions of nitro-compound and phenol. It crystallises from alcohol in deep reddish-brown needles melting at 166°:

0·1057 gave 10·8 c.c. N_2 at 21° and 690 mm. N = 10·65.

$C_{20}H_{13}O_7N_3$ requires N = 10·3 per cent.

The ethyl ether also forms an *additive* compound,

$$C_{14}H_9{\cdot}OEt,C_6H_3(NO_2)_3,$$

which crystallises from benzene in minute, brick-red prisms melting at 147°:

0·1742 gave 15·8 c.c. N_2 at 21° and 690 mm. N = 9·45.

$C_{22}H_{17}O_7N_3$ requires N = 9·7 per cent.

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[*Received, August 15th*, 1916.]

CII.—*The Estimation of Arsenic in Organic Compounds.*

By Arthur James Ewins.

In the course of some experiments on the fate of diaminodihydroxyarsenobenzene (salvarsan) in the animal organism, the author's attention was drawn to a method of estimating arsenic in organic tissues which was devised by Norton and Koch (*J. Amer. Chem. Soc.*, 1905, **27**, 1247), and successfully employed by them and others. The principle was essentially that of Kjeldahl's method of the determination of nitrogen adapted to the estimation of arsenic (or antimony), and its employment in the investigation referred to above gave entirely satisfactory results.

For some time past Dr. Barger and the author have been engaged in an investigation dealing with a number of organic derivatives of arsenic, the results of which they hope to publish in due course. It occurred to the author that Norton and Koch's method might be applied to the estimation of arsenic in such compounds, more particularly as the methods which are to be found in the literature are generally more or less complicated. These involve, for example, such processes as fusion, distillation under certain conditions, and subsequent estimation of arsenic by gravimetric and volumetric methods (Little, Morgan, and Cahen, T., 1909, **95**, 1477; Warunis, *Chem. Zeit.*, 1912, **31**, 1205; Böhrisch and Küschner, *Pharm. Zentr.-h.*, 1911, **52**, 1365, and numerous further references to be found in these publications).

A comparatively simple and rapid method of determining arsenic in salvarsan and neosalvarsan has been described by Lehmann (*Apoth. Zeit.*, 1912, **27**, 545).

The substance is completely oxidised by means of permanganate and concentrated sulphuric acid, the product further treated with hydrogen peroxide, and the arsenic finally estimated volumetrically by the amount of iodine liberated from an acid solution containing potassium iodide. The method is rapid (one to one and a-half hours for the estimation), and gives accurate results with the compounds mentioned and certain closely allied derivatives provided adequate precautions are taken to ensure the complete elimination of excess of hydrogen peroxide (merely boiling is insufficient in the author's experience). In the case of a number of arsenic derivatives which have been examined, however, the method entirely fails, owing to the fact that preliminary treatment with potassium permanganate and sulphuric acid does not

bring about complete oxidation. As examples of such derivatives may be mentioned benzarsinic acid and dimethyl- and diethyl-benzarsinic acids.

In view of the foregoing, therefore, experiments were made in order to test the applicability of the Norton-Koch method to such compounds. After a few trials, the conditions necessary for accurate estimations were arrived at, and the method as described below has now been used for some months. Quite satisfactory results have been obtained with arsenic derivatives of widely differing constitution. The advantages of the method are that it requires only the simplest apparatus and materials, needs very little attention, and is applicable to all but very volatile arsenic derivatives. Essentially the method consists in the moist combustion of the organic compounds by means of concentrated sulphuric acid. During the process the arsenic present is converted into arsenious acid, which is finally estimated volumetrically by means of iodine in the usual manner. The details of the method are as follows:

A small quantity of the substance (0·1 to 0·2 gram) is accurately weighed and washed into a long-necked Kjeldahl flask of about 300 c.c. capacity. Ten grams of potassium sulphate and 0·2 to 0·3 gram of starch (which can, after a little experience, be sufficiently accurately estimated and need not be weighed) are then added. Any solid adhering to the neck of the flask is washed in with a little water. Twenty c.c. of concentrated sulphuric acid are next cautiously added, and the flask is then placed on a wire gauze over a Bunsen flame. As soon as the contents of the flask begin to froth the flame is lowered somewhat until the frothing diminishes, which generally happens within about ten to fifteen minutes from the commencement of heating. The flame is then again turned on full, and heating continued until the liquid becomes colourless or of a very pale yellow tint. The flask is shaken once or twice during the heating in order to wash down any material adhering to the walls. The time required for the complete combustion of the material is usually about four hours, but during the greater part of this time the flask may safely be left without attention.

The contents of the flask are next allowed to cool, and then quantitatively washed into a flat-bottomed flask of about 350 c.c. capacity. A solution of sodium hydroxide (10—12*N*) is then added from a burette until the solution is just distinctly alkaline to litmus. (A small piece of litmus paper added to the contents of the flask serves as the most convenient indicator.)

The flask and its contents are then cooled to about 30—40°, and

a few drops of concentrated sulphuric acid added until the solution is again distinctly acid. (Care should be taken that no drops of the sodium hydroxide solution remain on the inside of the neck of the flask, which should be well washed down with water, or the flask may be closed and shaken.) A saturated solution of sodium hydrogen carbonate is next added from a burette until the solution becomes distinctly alkaline and an excess of 5—10 c.c. of the reagent is present.

To this solution is now added 2 c.c. of a 1 per cent. solution of starch, and the arsenious acid present is titrated by means of a $N/20$-solution of iodine. Towards the end of the titration the solution usually develops a reddish-violet tint, which obviously fades on keeping. The end-point, however, is only reached when the solution acquires the characteristic deep blue colour given by free iodine in the presence of starch. This blue colour, moreover, shows no tendency to fade on keeping. From the amount of iodine required, the percentage of arsenic present is easily calculated. One c.c. of $N/20$-iodine = 0·001875 gram of arsenic.

The following are the results of a series of determinations which were made to determine the accuracy of the method, and are quoted without selection.

Arsanilic Acid, $NH_2 \cdot C_6H_4 \cdot As(OH)_2O$. As = 34·56 per cent.

Weight of substance.	c.c. N 20-I.	As per cent. found.
0·1067	19·65	34·5
0·0767	14·2	34·7
0·1248	23·1	34·7
0·0760	14·0	34·6

Acetylarsanilic Acid, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot As(OH)_2O$. As = 29·1 per cent.

0·0880	13·65	29·1
0·1150	17·5	28·5
0·0888	13·7	28·9
0·0804	12·5	29·1

Diethylbenzarsinic Acid, $(C_2H_5)_2As \cdot C_6H_4 \cdot CO_2H$. As = 29·5 per cent.

0·0979	15·4	29·5
0·1342	20·95	29·3
0·1040	16·15	29·1

Diaminodihydroxyarsenobenzene (salvarsan),
$C_{12}H_{12}O_2N_2As_2,2HCl,2H_2O$. As = 31·6 per cent.*

	Weight of substance.	c.c. *N* 20-*I*.	As per cent. found.
Specimen (*a*)			
	0·0797	13·0	30·6
	0·1191	19·5	30·7
	0·1198	19·55	30·6
Specimen (*b*)			
	0·1020	17·0	31·25
	0·1220	20·5	31·5
	0·1214	20·5	31·6
Specimen (*c*)			
	0·1184	19·2	30·4
	0·0776	12·6	30·4
Specimen (*d*)			
	0·0972	15·8	30·5
	0·1232	19·9	30·3

* The commercial samples of salvarsan contain impurities and vary from one to another in respect of their arsenic content. In no case does the composition of the product agree exactly with the formula indicated.

In addition, the following are some results obtained with other substances which have been involved in the work already referred to:

Formula of substance.	Weight taken.	c.c. *N*/20-*I*.	As per cent. Found.	As per cent. Calculated.
$(OH)_2OAs{\cdot}C_6H_4{\cdot}CN$	0·1312	22·7	32·9	33·0
$(OH)_2OAs{\cdot}C_6H_2(NO_2)_2{\cdot}CN$	0·1118	14·2	23·8	23·5
$(OH)_2OAs{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$	0·1137	18·3	30·2	30·7
$(OH)_2OAs{\cdot}C_6H_2(NO_2)_2{\cdot}OH$	0·1414	18·9	25·0	24·5
$(OH)_2OAs{\cdot}C_6H_3{:}O_2{:}CH_2$	0·1207	19·9	30·8	30·5
$(OH)_2OAs{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	0·0365	5·9	30·3	30·6
$(OH)_2OAs{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2NHBz$	0·1482	16·5	20·9	21·4
$(OH)_2As{\cdot}C_6H_4{\cdot}CN$	0·1105	21·0	35·6	35·5
$OAs{\cdot}C_6H_4{\cdot}CN$	0·1368	28·0	38·4	38·7
$Cl_2As{\cdot}C_6H_4{\cdot}CN$	0·1200	18·8	29·4	29·6
$(CH_3)_2As{\cdot}C_6H_4{\cdot}CO_2H$	0·1121	19·9	33·3	33·2
$(CH_3)_2As{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$	0·1006	18·0	33·5	33·3
$(CH_3)_2As{\cdot}C_6H_4Bz$	0·1015	13·5	25·0	24·8
$(C_6H_5)_2As{\cdot}C_6H_4Bz$	0·1072	10·4	18·2	18·3
$(CH_3)_2OH(NO_3)As{\cdot}C_6H_4{\cdot}CO_2H$	0·1496	19·9	24·9	24·8

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CIII.—*Overvoltage Tables. Part IV. The Theories of Overvoltage and Passivity.*

By Edgar Newbery.

It was suggested some time ago (T., 1914, **105**, 2434) that overvoltage is due to three factors, namely, (1) Supersaturation of the metal surface with non-electrified gas under very high pressure due to the permeability of the metal to the ionised gas, but non-permeability to the molecular. (2) Deficiency or excess of non-hydrated ions (or atoms) in the immediate neighbourhood of the electrodes, and (3) Inductive action of the escaping ionised gas on the electrodes.

Further experience gained during the construction of these tables has convinced the author that the above theory is insufficient to account for all the observed phenomena. The chief objections are as follows:

(*a*) The overvoltage of an amalgamated zinc cathode rises to 0·88 volt with low current density and keeps this value for an indefinite time. The fraction of this overvoltage due to factor (2) above must be very small for reasons to be given later. The pressure, calculated from Nernst's equation, which is needed to produce this overvoltage is greater than 10^{30} atmospheres. Whilst it is certain that the surface-tension forces at the electrode surface must be very great, and further that Nernst's equation must be greatly modified for such high overvoltages, yet the pressures which must be assumed according to this theory are incredibly great.

(*b*) The postulation of a surface permeable to ions but not to molecules is to a great extent unjustifiable.

(*c*) The degree of deficiency or excess of non-hydrated ions or free atoms in the neighbourhood of the electrodes must be independent of the nature of the electrode, and any hydrogen overvoltage thus produced must be common to all electrodes. Rhodium at moderate current densities has a hydrogen overvoltage of 0·01 volt, and this value is therefore the maximum which can be allowed as the share of factor (2) in producing the total hydrogen overvoltage at any electrode.

Further, the excess or deficiency of the metastable products should be approximately proportional to the current density, and at indefinitely low current densities overvoltage from this source should be absent. The metal overvoltage of zinc only varied by 0·007 volt when the current density was changed from 10 to 2000 milliamperes per sq. cm. In the case of metal overvoltages, therefore, the influence of factor (2) in the above theory may also be

negligible. It is therefore advisable to recognise this factor as unimportant in the general theory of overvoltage, and to look for other reasons to account for metal overvoltage.

(*d*) A mathematical consideration of the possible inductive effect of the escaping ionised gas on the electrode with the aid of the data given (T., 1914, **105**, 2428 *et seq.*) shows that whilst a considerable effect may be produced, yet this alone is insufficient to account for the whole of the great lowering of overvoltage sometimes observed at high current densities.

(*e*) It is impossible to explain the relation of overvoltage to the periodic law by means of the mechanical considerations involved in the older theory.

It appears, therefore, that the two sets of forces referred to in Part III. of this series are physical and chemical respectively, the physical forces consisting in changes of pressure, solubility, and degree of ionisation of the gases present, and the chemical in the formation of definite compounds between the discharged ion and the electrode or some part of the electrode. These two sets of forces will now be considered separately.

(1) *Physical Forces in Overvoltage.*—The theory that all metals cooled from the liquid state consist of crystals cemented together by amorphous material is now generally accepted. Andrew and Holt (*Proc. Roy. Soc.*, 1913, [*A*], **89**, 170, and *Trans. Faraday Soc.*, 1914, **9**, 321) have shown that amorphous palladium and iron absorb and give up hydrogen much more rapidly than the crystalline variety, and there appears no reason to doubt that this property is general for all metals and gases, although to a greatly varying degree.

Treatment of a metal as cathode in dilute acid is equivalent to the application of extremely high pressures of hydrogen, and this hydrogen will certainly dissolve in the amorphous metal between the crystals. If the pressure is continued, the supersaturated metal near the surface will pass on some of the contained gas to other amorphous material further below the surface, and the expansion thus produced not only generates great internal pressures, but also weakens the cohesion between the crystals, with the result that surface disintegration is produced, followed by liberation of compressed gas which, in forcing its way out, forms the small craters of which photographs have been shown (T., 1914, **105**, 2427). The average diameter of these craters, by determining the size of the escaping bubbles, will also determine the degree of ionisation of the gas; the smaller the craters the greater will be the ionisation.

Certain metals, for example, zinc, thallium, or rhodium in acid, show very small changes of overvoltage under the most varied con-

ditions of current density and time, and since the physical forces applied are the same with these metals as with any others, the conclusion must be drawn that only small variations of overvoltage can be accounted for by such considerations. The small fall of overvoltage generally observed at high current densities is probably produced by the inductive action of the escaping ionised gas, whilst other causes must be looked for to account for the greater depressions produced with electrodes, such as silver, mercury, etc.

(2) *Chemical Forces in Overvoltage.*—It appears to be impossible to explain the close connexion between overvoltage and valency except by the assumption that definite compounds of the discharged ion with the electrode are formed. The single potentials of the normal oxides of the metals are quite independent of the valency of these metals, for example, the single potential of gold coated with oxide is very different from that of copper similarly treated.

A certain degree of regularity may, however, be observed in the single potentials of the higher oxides of some metals. Thus Müller and Spitzer (*Zeitsch. anorg. Chem.*, 1906, **50**, 343) found that platinum plates coated with the oxides of iron, nickel, or cobalt behaved in the same way as passive electrodes of the metals themselves when subjected to anodic polarisation in sodium hydroxide. Again, a platinum plate coated with lead dioxide shows little or no difference of potential from that of an accumulator anode plate in the same electrolyte.

It is not improbable, therefore, that anodic overvoltage is due to the formation of higher oxides on the surface of the electrode, which in most cases are only stable under the influence of the great pressures set up within the electrode during electrolysis.

In the same way cathodic overvoltage is probably due to the high single potential of metallic hydrides formed under similar conditions.

The following observations strongly support this theory:

(1) In cases where higher oxides are capable of independent existence these oxides are actually produced at anodes of the given metals, for example, lead dioxide on a lead anode, chromium trioxide on a chromium anode, etc.

(2) Hydrogen liberated from an antimony cathode in acid electrolyte contains a considerable percentage of stibine.

(3) Hydrogen liberated from a carbon cathode contains appreciable quantities of hydrocarbon, the nature of which has not yet been determined.

(4) Fowler (*Trans. Roy. Soc.*, 1909, **209**, 447), observing the arc spectrum of magnesium, found that a great number of lines in the

sun-spot spectrum were reproduced in that of a magnesium arc in an atmosphere of hydrogen. These lines are not found in the spectra of hydrogen or magnesium separately, and Fowler therefore concludes very reasonably that they are due to an unstable hydride of magnesium.

Evans (*Phil. Mag.*, 1916, [vi], **31**, 55), working with metallic cadmium, found that the pure metal heated to 800—1000° in a vacuum or in the presence of traces of oxygen gave a true line absorption spectrum, the oxide being non-volatile under these conditions, but on the admission of pure hydrogen a banded spectrum was obtained, indicating the presence of a gaseous compound. Here, again, we see strong indications of the existence of a hydride stable only at high temperatures, and therefore in all probability an endothermic compound.

If the hydrides formed during electrolysis are all endothermic, their high single potentials are easily understood.

(5) Copper hydride is a fairly stable substance, and is probably formed in appreciable quantity on the surface of a copper cathode. Mercury hydride is unknown in the free state and is probably decomposed at once when the applied cathodic potential is removed. An attempt was made to compare the absorbing powers of these two metals for hydrogen by charging a cathode of each until the overvoltage rose to a maximum and then discharging by connecting with a large electrode of the same metal through a high resistance and a galvanometer. It was found that although the mercury had a much greater overvoltage than the copper, the total current (and hence the total hydrogen) obtained from the copper was many times greater than that from the mercury. Hence it appears that considerable quantities of copper hydride are formed on the surface of a copper cathode.

The hydrides of the metals which are formed during cathodic polarisation must be considered to exert a solution pressure and to ionise in the same way as a metal. The ionisation of lead peroxide in this way has already been mentioned.

Again, these hydrides will, in most cases, form solid solutions in the electrode, and the form of the overvoltage curve will depend on the miscibility of the hydrides with the electrode substance. If the hydrides in question are almost immiscible with the electrode substance we may expect either a very definite overvoltage with very small variations due to current density or time, or else sudden, rapid "jumps" from one value to another when a particular hydride is formed or disappears. These two cases are best illustrated by the behaviour of thallium and iridium electrodes respectively.

The opposite case of extreme miscibility is well exhibited by the behaviour of retort carbon or mercury, as might have been expected from the nature of these substances. It is quite possible that the alternate formation and decomposition of substances of this nature which are only stable under the influence of electrical pressure or of high temperatures is the real source of part at least of the so-called thermionic currents from incandescent tungsten, carbon, etc. Langmuir (*J. Amer. Electrochem. Soc.*, 1916, **29**) states that unmistakable passivity phenomena occur in gas reactions at low pressures, and he also considers that passivity, overvoltage, catalysis, and the emission of electrons are only special cases of the same surface phenomena.

Composition of the Hypothetical Hydrides.

Although the subject is not yet sufficiently developed for a final decision as to the exact composition of these hydrides, the following theory satisfactorily explains all the phenomena observed up to the present.

(1) The hydrides which show the group overvoltage are the lowest formed by the metals in each group. It will therefore be assumed for the present that they have the formula MH.

(2) The addition of an atom of hydrogen to any hydride changes its potential to that of the hydrides in the preceding group.

The hydrides showing the group overvoltages will therefore be as follows:

Group—							
1.	2.	3.	4.	5.	6.	7.	8.
Overvoltage—							
0·35	0·70	0·50	0·45	0·42	0·32	0·25	0·18
Hydride—							
$M^{I}H'$	$M^{II}H$	$M^{III}H'$	$M^{IV}H'$	$M^{V}H'$	$M^{VI}H'$	$M^{VII}H'$	$M^{VIII}H'_4$
$(M^{II}H'_2)$	$(M^{III}H'_3)$	$(M^{IV}H'_2)$	$M^{V}H'_2$	$M^{VI}H'_2$	$(M^{VII}H'_2)$	$M^{VIII}H_2$	
$(M^{III}H'_3)$	$M^{IV}H'_3$	$M^{V}H'_3$	$(M^{VI}H'_3)$	$(M^{VII}H'_3)$	$M^{VIII}H'_3$		
$(M^{IV}H'_4)$	$M^{V}H'_4$	$M^{VI}H'_4$	$(M^{VII}H'_4)$	$(M^{VIII}H'_4)$			
$(M^{V}H'_5)$	$(M^{VI}H'_5)$	$(M^{VII}H'_5)$	$M^{VIII}H'_5$				
$(M^{VI}H'_6)$	$M^{VII}H'_6$	$(M^{VIII}H_6)$					
$(M^{VII}H'_7)$	$M^{VIII}H'_7$						
$(M^{VIII}H'_8)$							

The values corresponding with the hydrides given in brackets in the above table have not been actually observed, although with the exception of those in group 1 there is no apparent reason why they should not be obtained under suitable conditions. In the remaining groups it may be remarked that about two-thirds of the theoretically possible values have been experimentally produced.

The potentials of the hydrides are thus determined by the number of unsatisfied valency bonds, and assuming that the maximum number of hydrogen atoms is given by the group number of the

elements, it is evident that no element other than those in group 8 can show the overvoltage typical of this group: a conclusion fully justified by experiment.

When no compound is formed, the metal will merely behave as a hydrogen electrode and the overvoltage will be zero. This behaviour is most noticeable with the platinum metals, which are therefore merely showing their usual reluctance to form compounds.

When conditions are arranged in such a way that hydrogen tends to enter the metal and form higher hydrides, the most stable hydride will be that which has the highest potential, since the latter will always be less than the applied potential. When all the valency bonds except one have been satisfied, the metal acquires the overvoltage typical of group 2. Further than this it cannot go, since to do so would decrease, and not increase, the potential, thus producing conditions further from those necessary for equilibrium. This explains the large number of metals which can acquire the high group 2 overvoltage, and also the entire absence of other metals from the list for group 1.

The mere solution of hydrogen in a metal has apparently no direct effect on the overvoltage, as may be concluded from the fact that solutions of hydrogen in platinum and palladium have the same single potential, although the concentration of gas in the latter is many times as great as in the former.

Whether the complex ions formed by cathodic treatment in alkali contain the alkali metal or not is still an open question, although the available evidence seems to indicate that both sodium and hydrogen are present in most cases, and that the presence of combined sodium excites greater activity of the remaining valency bonds. This may be the reason why zero overvoltages are unobtainable in alkali with any metal other than rhodium.

The fall of overvoltage to almost zero which is observed with several metals at the highest current densities is probably caused in part by diminution in the concentration of monatomic hydrogen in these circumstances. Only active hydrogen is capable of forming the compounds which produce the overvoltage, and if the current density is very high and the tendency to form these compounds not too marked, then the incoming hydrogen ions will be discharged so close to each other that the resultant atoms will more readily unite with each other than with the electrode material. In extreme cases, therefore, no compound will be formed and the overvoltage will sink to zero.

Metal overvoltages are probably produced in the same way as gas overvoltages by the formation of solid solutions of hydrides in the metal deposited on the cathode and of peroxides, etc., at

the anode. The occlusion of hydrogen in all electro-deposited metals is well known.

Metal and hydrogen are deposited together in a ratio which depends on the current density and the separation potentials, velocities, concentrations, and rate of dehydration of the ions, etc. Hence metal overvoltages may vary greatly in different solutions, although in the same solution the single potential of the solid solution of metallic hydride may be very constant if the temperature is constant.

On the other hand, the great variability of metal overvoltages, both cathodic and anodic, with change of temperature is easily accounted for by the variations in the rate of removal of hydrogen, oxygen, etc., from the electrode by the action of the metal or metallic salt present.

Further work on metal overvoltages is being carried out.

Anodic Overvoltage and Passivity.

If cathodic overvoltage is due to the presence of hydrides, then anodic overvoltage must be due to the presence of oxides, which in the majority of cases are only stable under high pressures. Passivity is produced when these higher oxides are good conductors of electricity and also insoluble or nearly so in the electrolyte. Valve action is produced when the oxides are insoluble in the electrolyte, but bad conductors of electricity. The degree of passivity and the efficiency of the valve action is therefore determined by the insolubility and conductivity of these oxides, and is not directly dependent on their single potentials (that is, on the anodic overvoltage). Further, it is not necessary to specify oxygen as the sole producer of anodic overvoltage or passivity, since it is well known that anodic overvoltage is obtainable in hydrochloric acid, etc., and Hittorf has passivated chromium by anodic treatment in hydriodic acid. In certain cases it is possible that the film of oxide covers only the more readily soluble, amorphous phase, leaving the sparingly soluble, crystalline phase exposed to the slow action of the electrolyte, and in such cases the reflecting power of the surface would be almost unaffected.

The above is, of course, only a slightly modified form of the "oxide film" theory of Faraday, which has been so often attacked but still finds many supporters.

The statement which has most discredited this theory is that of Müller and Koenigsberger (*Zeitsch. Elektrochem.*, 1907, **13**, 659), who state that the reflecting power of an iron surface is unaltered by passivation. In addition to the fact already shown that this, even if true, does not necessarily invalidate the oxide

film theory, the experimental method adopted for proving the above statement is open to grave objection. Two iron plates were placed in a given electrolyte and a current passed between them liberating hydrogen from one and rendering the other passive. No difference of reflecting power was observable between the two plates before and after treatment in this manner, and the above statement was then based on the unjustifiable assumption that the cathode was unchanged. The disintegrating effect of cathodic treatment previously illustrated (T., 1914, **105**, 2427) was unknown at that time, and this experiment only shows therefore that the reflecting powers of anode and cathode were altered to the same extent under the given conditions.

A pure iron electrode treated anodically with a low current density in dilute sulphuric acid soon acquires a brilliant reflecting surface. If now the current density is increased until passivity is produced, the surface is at once dulled to a degree clearly visible without the aid of instruments.

If the protecting oxide is non-conducting, it becomes impossible to measure the anodic overvoltage of the metal. The resistance of the film rises as the thickness increases and the current sinks to a value approaching zero. At the same time a condenser is produced, the non-conducting oxide acting as the dielectric, and since this condenser charges when the current is passed and then discharges through the potentiometer circuit, apparent overvoltages of almost unlimited value are obtained.

The reason why nearly all metals can be rendered passive by anodic treatment in sodium hydroxide solution, whilst very few can be passivated in dilute sulphuric acid, is due partly to the much greater number of oxygen and hydroxyl ions present in the former electrolyte and partly to the greater solubility of most metallic oxides in the latter.

The fact that so many of the anodically formed oxides are good electrical conductors is additional evidence of the probability that they ionise like a metal.

If the protecting oxide is a conductor having a markedly higher resistance than the metal, and if it is also sparingly soluble in the electrolyte, then we have the possibility of the periodic activation and passivation which is most easily produced with a nickel anode in dilute sulphuric acid, and less readily with anodes of iron or silver.

When the applied electromotive force produces a current which generates the protecting oxide rather more slowly than it is dissolved by the electrolyte, the film becomes thinner and finally breaks at one or more points. A sudden rush of current then

occurs which rapidly regenerates the protective coating, whereupon the resistance rises and the current falls again.

A careful observation of the potential and current density at a nickel anode when this periodic variation occurs will show that its behaviour corresponds in every detail with that described above.

These phenomena afford perhaps the most conclusive evidence in favour of Faraday's oxide-film theory of passivity.

The chemical stability of the higher oxides and hydrides in question is not to be measured by the overvoltage potentials. Thus lead peroxide is far more stable than the platinum oxides, and yet the overvoltage of lead (anodic) is higher than that of platinum. Similarly, copper hydride is one of the most stable of the metallic hydrides, although copper has approximately the same overvoltage as silver or gold, the hydrides of which only exist under pressure. This chemical stability is of great importance when these electrodes are used for treatment of substances which are only oxidised or reduced slowly, and it is quite possible that in such cases an electrode that produces a comparatively stable hydride may effect reductions which another electrode of higher overvoltage is unable to do. Thus under certain conditions oleic acid may be reduced with the aid of a copper electrode, whilst a lead electrode fails. This may also explain why a copper electrode reduces nitrates in acid solution to ammonia whilst a lead cathode produces large quantities of hydroxylamine.

Summary of Work in Parts I.–IV. of this Series.

(1) The overvoltage, cathodic and anodic, of a number of electrodes has been measured in acid and in alkali under varying conditions of time and current density.

(2) Elements in the same group of the periodic system show the same overvoltage.

(3) When the overvoltage of a metal changes in such a way as to correspond with the typical overvoltage of another group, compounds of that metal are generally known in which the metal has the valency characteristic of the new group.

(4) Overvoltage is probably due to the high solution potentials of compounds of the electrode material with the discharged ion or with a product of the discharged ion. These compounds tend to form solid solutions in the electrode substance, and are usually stable only under the influence of high pressures or high temperatures.

(5) A slight fall of overvoltage is produced by the inductive action of escaping ionised gas at high current densities, whilst greater diminution of the overvoltage is produced by breakage of

the electrode surface, release of internal pressures, and subsequent decomposition of the compounds present.

(6) It is probable that compounds of the nature described play a considerable part in the production of thermionic currents.

(7) Passivity is due to the insolubility and good electrical conductivity of the above compounds which form a protective coating either over the whole metal surface or over the more easily soluble amorphous phase only. The coating may consist of the pure compound or of a solid solution of the compound in the electrode substance.

(8) The chemical stability of the higher oxides or hydrides formed on the surface of the electrode is of greater importance than the overvoltage when dealing with substances which are only oxidised or reduced with a low velocity.

In conclusion, the author wishes to express his thanks to Prof. Edwards, of the Metallurgical Department of this University, for many useful suggestions, and especially to Prof. Lapworth, of the Chemical Department, for his valuable criticisms and encouragement in this work.

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[*Received, October 14th*, 1916.]

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FORMULA INDEX.

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The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

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CH_3I Methyl iodide, reactions of metallic cyanides with (Hartley), 1296.

CO_8N_4 Tetranitromethane, action of, with potassium ferrocyanide (Chattaway and Harrison), 171.

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CHNS Thiocyanic acid, cupric salt, action of water on (Philip and Bramley), 597.

CH_4ON_2 Carbamide, reaction of acetic anhydride with (Werner), 1120.

CH_4N_2S Thiocarbamide, reaction of acetic anhydride with, and its potassium salt (Werner), 1120.

CO_6N_3Br Bromotrinitromethane, reaction of, with potassium ferrocyanide (Chattaway and Harrison), 171.

1 V

CH_3O_2NSHg Mercury methyl-mercaptide nitrite (Rây), 134.

C_2 Group.

C_2HN_5 5-Diazo-1:2:4-triazole, aurichloride of (Morgan and Reilly), 159.

C_2H_5Br Ethyl bromide, preparation of (Holt), 1.

2 III

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$C_2H_4N_2S$ Substance, from formaldehyde and thiocarbamide (Dixon and Taylor), 1253.

C_2H_5NS Thioacetamide, action of iodine on (Rây and Dey), 698.

2 IV

C_2H_4ONK Potassium acetamide, decomposition of (RAKSHIT), 180.

2 V

$C_2H_5O_2NSHg$ Mercury ethyl-mercaptide nitrite (RÂY), 133.

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3 III

$C_3H_4ON_2$ Acetylcyanamide, silver salt (WERNER), 1130.

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$C_3H_8N_4S_2$ Substance, from methylene di-iodide and thiocarbamide (DIXON and TAYLOR), 1255.

3 IV

$C_3H_9O_2NS$ Trimethylsulphonium nitrite (ADDY and MACBETH), 756.

3 V

$C_3H_4O_2NS_2Hg$ Mercury 2-mercaptothiazoline nitrite (RÂY), 607.

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$C_4H_6O_5$ Malic acid, metallic salts of (PICKERING), 236.

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$C_4H_7O_2N$ β-Aminocrotonic acid, alkylation of derivatives of (ROBINSON), 1038.

4 IV

$C_4H_4O_2NNa$ Sodium diacetamide, decomposition of (RAKSHIT), 180.

$C_4H_{11}I_3S_2Hg$ Substance, from mercury methyl-mercaptide nitrite and ethyl iodide (RÂY), 137.

4 V

$C_4H_{10}O_8N_2S_2Hg_2$ Substance, from ethyl disulphide and mercuric nitrite (RÂY), 137.

C_5 Group.

C_5H_5N Pyridine, action of, with alkyl nitrites (ADDY and MACBETH), 754.

5 III

C_5H_5ON Pyrrole-2-aldehyde, condensation of ketones with (LUBRZYNSKA), 1118.

$C_5H_5ON_3$ Glyoxaline-4(or 5)-formaldehydecyanohydrin (PYMAN), 197.

$C_5H_6O_2N_2$ Methyl glyoxaline-4(or 5)-carboxylate (PYMAN), 200.

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$C_5H_9ON_3$ β-Hydroxy-β-glyoxaline-4(or 5)-ethylamine, and its salts (PYMAN), 197.

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C_6H_6O Phenol, density and viscosity of mixtures containing (BRAMLEY), 10.

$C_6H_6S_2$ Dithioresorcinol, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.

$C_6H_8O_7$ Citric acid, metallic salts of (PICKERING), 236.

$C_6H_{10}O_3$ Ethyl acetoacetate, alkylation of (ROBINSON), 1038.

$C_6H_{12}O_3$ Paracetaldehyde, estimation of mixtures of acetal and (ORTON and MCKIE), 184.

$C_6H_{12}O_6$ Laevulose, new variety of (IRVINE and ROBERTSON), 1305; mutarotation of (PATTERSON), 1225.

$C_6H_{14}O_2$ Acetal, estimation of mixtures of paracetaldehyde and (ORTON and MCKIE), 184.

6 III

$C_6H_3O_6N_3$ *s*-Trinitrobenzene, additive compounds of (SUDBOROUGH), 1339; (CADRE and SUDBOROUGH), 1349; additive compounds of, with heterocylic compounds containing nitrogen in the ring (SASTRY), 270.

$C_6H_4N_6Fe$ Hydroferrocyanic acid, potassium salt, action of, with bromotrinitromethane and tetranitromethane (CHATTAWAY and HARRISON), 171.

$C_6H_6N_2Cl_2$ 3:5-Dichlorophenylhydrazine, and its hydrochloride (CHATTAWAY and ELLINGTON), 588.

$C_6H_6N_2Br_2$ 3:5-Dibromophenylhydrazine, and its hydrochloride (CHATTAWAY and ELLINGTON), 588.

$C_6H_8O_2N_2$ Ethyl glyoxaline-4(or 5)-carboxylate (PYMAN), 200.

$C_6H_9O_2N_3$ Histidine, synthesis of (PYMAN), 186.

6 IV

$C_6H_{10}O_2N_2S$ Substance, from carbethoxythiocarbimide and aldehyde–ammonia (DIXON and TAYLOR), 1260.

$C_6H_{12}ON_2S$ Substance, from allylthiocarbamide and acetaldehyde (DIXON and TAYLOR), 1255.

$C_6H_{15}O_2NS$ Triethylsulphonium nitrite (ADDY and MACBETH), 757.

$C_6H_{15}I_3S_2Hg$ Ethyldisulphoniummercuri-iodide (RÂY), 135, 611.

C_7 Group.

$C_7H_6O_5$ Gallic acid, oxidation of (BLEULER and PERKIN), 529.

$C_7H_8O_2$ *iso*Homocatechol (PERKIN), 920.

7 III

C_7H_6ClBr *o*-Chlorobenzyl bromide (LEONARD), 570.

$C_7H_9N_2Br$ Bromotolylhydrazines (CHATTAWAY and HODGSON), 582.

$C_7H_{10}ON_2$ 3:5-Diaminoanisole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

7 IV

$C_7H_6O_3NI$ 4-Iodo-2-nitroanisole (ROBINSON), 1084.

$C_7H_{17}I_3S_2Hg$ Substance, from mercury ethyl-mercaptide nitrite and *n*-propyl iodide (RÂY), 137.

C_8 Group.

$C_8H_8O_3$ 5:6-Dihydroxy-*o*-tolualdehyde (PERKIN), 913.

$C_8H_8O_4$ 5:6-Dihydroxy-*o*-toluic acid (PERKIN), 919.

8 III

$C_8H_6O_6N_2$ Dinitro-2:3-methylenedioxytoluene (PERKIN), 912.

$C_8H_6O_2Br_2$ Dibromo-2:3-methylenedioxytoluene (PERKIN), 918.

$C_8H_7O_2N$ Aminophthalide (TCHERNIAC), 1243.

$C_8H_7O_2Cl$ Phenylchloroacetic acid, conversion of, to phenylaminoacetic acid (SENTER and DREW), 1091.

$C_8H_7O_2Br$ Phenylbromoacetic acid, kinetics and dissociation constant of (SENTER and TUCKER), 690.

$C_8H_7O_8N_3$ 2:3:6-Trinitro-5-hydroxy-*p*-tolyl methyl ether (ROBINSON), 1089.

$C_8H_9O_2N$ Phenylaminoacetic acid, conversion of phenylchloroacetic acid to (SENTER and DREW), 1091.

$C_8H_8O_5N_2$ 2:5-Dinitro-*p*-tolyl methyl ether (ROBINSON), 1089.

$C_8H_8N_2S$ Substance, from phenylthiocarbamide and formaldehyde (DIXON and TAYLOR), 1256.

C_8H_9ON Substance, from pyrrole-2-aldehyde and acetone (LUBRZYNSKA), 1119.

$C_8H_9O_3N$ 5:6-Dihydroxy-*o*-tolualdoxime (PERKIN), 914.

C_8H_9OI 3- and 5-Iodo-*o*-tolyl methyl ethers (ROBINSON), 1080.

$C_8H_{10}ON_4$ 4(or 5)-[Glyoxaline-4(or 5)-methyl]-glyoxaline-5(or 4)-methyl alcohol, and its salts (PYMAN), 200.

8 IV

$C_8H_5O_3NBr_2$ 2:4-Dibromo-oxanilic acid (+ H_2O) (CHATTAWAY and CLEMO), 100.

$C_8H_6O_2N_2Br_2$ 2:4-Dibromo-oxanilamide (CHATTAWAY and CLEMO), 101.

$C_8H_7O_2NCl_2$ Methyl 2:4-dichlorocarbanilate (CHATTAWAY and CLEMO), 98.

$C_8H_7O_6SNa$ Substance, from phthalonic acid, sodium hydroxide and sulphur dioxide (TCHERNIAC), 1242.

$C_8H_8ON_2Cl_2$ Acetyl-3:5-dichlorophenylhydrazine (CHATTAWAY and ELLINGTON), 589.

$C_8H_8ON_2Br_2$ Acetyl-3:5-dibromophenylhydrazine (CHATTAWAY and ELLINGTON), 589.

$C_8H_8O_3NI$ 3-Iodo-5- and -6-nitro-*o*- and -*p*-tolyl methyl ethers (ROBINSON), 1085.

$C_8H_8O_4NI$ 2-Iodo-5-nitroquinol dimethyl ether (ROBINSON), 1087.
4-Iodo-5-nitroveratrole (ROBINSON), 1087.

$C_8H_{18}OClP$ Chlorotriethylphosphinoacetaldehyde, and its platinichloride (CALDWELL), 283.

$C_8H_{18}OBrP$ Bromotriethylphosphinoacetaldehyde (CALDWELL), 283.

8 V

$C_8H_5O_3NClBr$ Chlorobromo-oxanilic acids (CHATTAWAY and CLEMO), 99.

$C_8H_6O_2N_2ClBr$ Chlorobromo-oxanilamides (CHATTAWAY and CLEMO), 100.

$C_8H_7O_2NClBr$ Methyl chlorobromocarbanilates (CHATTAWAY and CLEMO), 97.

$C_8H_{13}N_3I_3S_4Hg$ Substance, from mercury mercaptothiazoline nitrite and ethyl iodide (RÂY), 608.

C_9 Group.

$C_9H_4O_4$ Phthalonic anhydride (TCHERNIAC), 1238.
$C_9H_6O_4$ 5:6-Carbonyldioxy-*o*-tolualdehyde (PERKIN), 913.
$C_9H_6O_5$ 5:6-Carbonyldioxy-*o*-toluic acid (PERKIN), 918.
Phthalonic acid, preparation of (TCHERNIAC), 1236.
$C_9H_8O_8$ Dihydroxyhemimellitic acid (DEAN and NIERENSTEIN), 594.
C_9H_7N Quinoline, action of, with alkyl nitrites (ADDY and MACBETH), 754.
$C_9H_8O_3$ 5:6-Methylenedioxy-*o*-tolualdehyde (PERKIN), 907.
$C_9H_8O_4$ 5:6-Methylenedioxy-*o*-toluic acid (PERKIN), 917.
$C_9H_8N_2$ 2- and 4-Aminoquinolines, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1347.
$C_9H_{10}O_3$ 6-Hydroxy-5-methoxy-*o*-tolualdehyde (PERKIN), 915.
$C_9H_{14}O$ Ketone, from oil of the Indian deodar tree (ROBERTS), 793.

9 III

C_9H_7ON Carbostyril, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.
$C_9H_7O_3N$ Amide of phthalidecarboxylic acid (TCHERNIAC), 1239.
$C_9H_7O_4N$ Phthalonamic acid (TCHERNIAC), 1239.
$C_9H_7O_5N$ 3-Nitro-5:6-methylenedioxy-*o*-tolualdehyde (PERKIN), 910.
$C_9H_7O_6N$ 3-Nitro-5:6-methylenedioxy-*o*-toluic acid (PERKIN), 913.
$C_9H_9O_3N$ 5:6-Methylenedioxy-*o*-tolualdoxime (PERKIN), 908.
$C_9H_9O_8N_3$ 2:5:6-Trinitrohomoveratrole (ROBINSON), 1090.
$C_9H_{10}O_6N_2$ 5:6-Dinitrohomoveratrole (ROBINSON), 1090.
$C_9H_{10}N_2S$ Substance, from phenylthiocarbamide and acetaldehyde (DIXON and TAYLOR), 1256.
$C_9H_{11}ON$ Substance, from pyrrole-2-aldehyde and methyl ethyl ketone (LUBRZYNSKA), 1120.
$C_9H_{11}O_3N_3$ 5:6-Dihydroxy-*o*-tolualdehydesemicarbazone (PERKIN), 914.
$C_9H_{12}O_2N_2$ Ethyl-3:5-diaminobenzoate, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

9 IV

$C_9H_5O_5N_2Cl_2$ Pyruvic acid 3:5-dichlorophenylhydrazone (CHATTAWAY and ELLINGTON), 593.
$C_9H_8O_2N_2Br_2$ 2:4-Dibromomalonanilamide (CHATTAWAY and CLEMO), 102.
Pyruvic acid 3:5-dibromophenylhydrazone (CHATTAWAY and ELLINGTON), 592.
$C_9H_9O_2NCl_2$ Ethyl 2:4-dichlorocarbanilate (CHATTAWAY and CLEMO), 98.
$C_9H_{10}ON_2S$ Substance, from phenylthiocarbamide and formaldehyde (DIXON and TAYLOR), 1256.

9 V

$C_9H_7O_3NClBr$ Chlorobromomalonanilic acids (CHATTAWAY and CLEMO), 102.
$C_9H_8O_2N_2ClBr$ Chlorobromomalonanilamides (CHATTAWAY and CLEMO), 102.
$C_9H_9O_2NClBr$ Ethyl chlorobromocarbanilates (CHATTAWAY and CLEMO), 97.

C_{10} Group.

$C_{10}H_8$ Naphthalene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

10 II

$C_{10}H_6Br_2$ α-Dibromonaphthalene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{10}H_7Br$ α-Bromonaphthalene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{10}H_8O_2$ 1:3-Dihydroxynaphthalene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{10}H_8O_3$ Phenylsuccinic anhydrides (WREN and WILLIAMS), 580.

$C_{10}H_8S$ Thionaphthol, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.

$C_{10}H_9N$ Phenylpyrrole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{10}H_{10}O_4$ Methyl 5:6-methylenedioxy-*o*-toluate (PERKIN), 917.

Phenylsuccinic acids, optically active (WREN and WILLIAMS), 572.

$C_{10}H_{10}O_5$ *m*-Opianic acid (PERKIN), 928.

$C_{10}H_{10}O_6$ *m*-Hemipinic acid, preparation of (PERKIN), 889.

$C_{10}H_{10}N_4$ Glyoxalineformaldehydephenylhydrazone (PYMAN), 193.

$C_{10}H_{12}O_3$ 5:3-Dimethoxy-*o*-tolualdehyde (PERKIN), 915.

$C_{10}H_{12}O_4$ 5:6-Dimethoxy-*o*-toluic acid (PERKIN), 920.

$C_{10}H_{13}N$ 6-Methyltetrahydroquinoline, additive compounds of trinitrobenzene and (SASTRY), 271.

$C_{10}H_{16}N_2$ Diethyl-*p*-phenylenediamine, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{10}H_{18}O_6$ Methylfructosidemonoacetone (IRVINE and ROBERTSON), 1313.

10 III

$C_{10}H_7O_4N$ α-Nitronaphthalene, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{10}H_9O_4N$ *m*-Hemipinimide (PERKIN), 892, 930.

m-Opianic acid oxime anhydride (PERKIN), 929.

$C_{10}H_{10}O_5N_2$ Carbethoxynitrobenzaldoximes (BRADY and DUNN), 678.

$C_{10}H_{11}O_2N_3$ 5:6-Methylenedioxy-*o*-tolualdehydesemicarbazone (PERKIN), 908.

$C_{10}H_{11}O_5N$ *m*-Opianic acid oxime (PERKIN), 929.

$C_{10}H_{13}O_3N$ 5:6-Dimethoxy-*o*-tolualdoxime (PERKIN), 916.

10 IV

$C_{10}H_9O_3NBr_2$ Ethyl 2:4-dibromo-oxanilate (CHATTAWAY and CLEMO), 100.

$C_{10}H_{11}O_2N_2Br$ Pyruvic acid 5-bromo-*o*-tolylhydrazone (CHATTAWAY and HODGSON), 586.

10 V

$C_{10}H_9O_3NClBr$ Ethyl chlorobromo-oxanilates (CHATTAWAY and CLEMO), 99.

$C_{10}H_{11}ONClBr$ *n*-Butyrochlorobromoanilides (CHATTAWAY and CLEMO), 93.

C_{11} Group.

$C_{11}H_{10}$ β-Methylnaphthalene, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

11 II

$C_{11}H_7N$ α- and β-Naphthonitriles, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{11}H_8O_2$ 2-Hydroxy-1-keto-4-methylene-1:4-dihydronaphthalene (DEAN and NIERENSTEIN), 593.

α-Naphthoic acid, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

β-Naphtholaldehyde, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{11}H_{10}O_5$ 4-Keto-5:6-dimethoxydihydro*iso*coumarin (PERKIN), 958.
$C_{11}H_{11}N$ Tolylpyrrole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.
$C_{11}H_{12}O_3$ 4:5-Dimethoxy-2-vinylbenzaldehyde (PERKIN), 905.
$C_{11}H_{12}O_5$ Lactone of 4:5-dimethoxyphenylacetaldehyde-2-carboxylic acid (PERKIN), 972.
$C_{11}H_{14}O_4$ ω-Hydroxy-3:4-dimethoxy-*o*-tolylacetaldehyde (PERKIN), 956.
Methyl 5:6-dimethoxy-*o*-toluate (PERKIN), 921.
$C_{11}H_{14}O_5$ ω-Hydroxy-3:4-dimethoxy-*o*-tolylacetic acid (PERKIN), 959.
$C_{11}H_{15}N$ 1-Ethyltetrahydroquinoline, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

11 III

$C_{11}H_{13}O_3N$ 4:5-Dimethoxy-2-vinylbenzaldoxime (PERKIN), 905.
$C_{11}H_{13}O_5N_3$ *m*-Opianic acid semicarbazone (PERKIN), 930.
$C_{11}H_{13}O_6N$ 3-Nitro-5:6-methylenedioxy-*o*-tolualdehydedimethylacetal (PERKIN), 911.
$C_{11}H_{15}O_3N_3$ 5:6-Dimethoxy-*o*-tolualdehydesemicarbazone (PERKIN), 916.
$C_{11}H_{15}O_4N$ ω-Hydroxy-3:4-dimethoxy-*o*-tolylacetaldoxime (PERKIN), 956.

11 IV

$C_{11}H_8O_2N_2Cl_2$ Citraconyl-3:5-dichlorophenylhydrazide (CHATTAWAY and ELLINGTON), 590.
$C_{11}H_8O_2N_2Br_2$ Citraconyl-3:5-dibromophenylhydrazide (CHATTAWAY and ELLINGTON), 590.

11 V

$C_{11}H_{11}O_3NClBr$ Ethyl chlorobromomalonanilate (CHATTAWAY and CLEMO), 102.

C_{12} Group.

$C_{12}H_8$ Acenaphthylene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.
$C_{12}H_{10}$ Acenaphthene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

12 II

$C_{12}H_8N_2$ Phenazine, compounds of trinitrobenzene and (SASTRY), 273.
$C_{12}H_{10}O$ 2-Methoxy-1:4-methylenenaphthalene (DEAN and NIERENSTEIN), 596.
α-Naphthyl methyl ketone, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.
$C_{12}H_{10}O_2$ Methyl α- and β-naphthoates, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1345.
2-Methoxy-1-keto-4-methylene-1:4-dihydronaphthalene (DEAN and NIERENSTEIN), 595.
$C_{12}H_{10}N_2$ 3-Aminocarbazole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.
$C_{12}H_{10}N_6$ 1:2:4-Triazole-5-azo-β-naphthylamine (MORGAN and REILLY), 159.
$C_{12}H_{11}N$ 9-Aminoacenaphthene, additive compound of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1353.
$C_{12}H_{12}O_3$ 1-Hydroxy-2-methoxynaphthyl-4-carbinol (DEAN and NIERENSTEIN), 595.
$C_{12}H_{12}O_6$ Acetyl-*m*-opianic acid (PERKIN), 931.
$C_{12}H_{12}N_2$ *p*-Aminodiphenylamine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{12}H_{14}O_4$ Methyl phenylsuccinates (WREN and WILLIAMS), 578.
$C_{12}H_{14}O_7$ Ethyl phloroglucinoldicarboxylate, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.
$C_{12}H_{18}O_8$ *iso*Butyl diacetyltartrate, rotation of (PATTERSON), 1139.
$C_{12}H_{22}O_{11}$ Sucrose, structure of (HAWORTH and LAW), 1314.

12 III

$C_{12}H_9ON_5$ 1:2:4-Triazole-5-azo-β-naphthol (MORGAN and REILLY), 159.
$C_{12}H_9NS$ Thiodiphenylamine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.
$C_{12}H_{12}N_2S_2$ *o*-Diaminodiphenyl disulphide, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.
$C_{12}H_{13}ON$ 2- and 4-Amino-1-naphthyl ethyl ethers, additive compounds of *s*-trinitrobenzene and (SUDBOROUGH), 1345.
$C_{12}H_{13}O_5N_3$ 4-Keto-5:6-dimethoxydihydro*iso*coumarinsemicarbazone (PERKIN), 958.
$C_{12}H_{13}O_6N$ 3:4-Dimethoxy-6-methylcarbamylphenylglyoxylic acid ($+2H_2O$) (PERKIN), 893.
$C_{12}H_{14}O_5N_2$ 5(or 8)-Nitro-6:7-dimethoxy-2-methyltetrahydro*iso*quinolone (PERKIN), 892.
$C_{12}H_{15}O_3N$ 6:7-Dimethoxy-2-methyltetrahydro*iso*quinolone (PERKIN), 889, 925.
$C_{12}H_{15}O_3N_3$ 4:5-Dimethoxy-2-vinylbenzaldehydesemicarbazone (PERKIN), 904.
$C_{12}H_{16}O_3N_2$ Carbethoxy-*p*-dimethylaminobenz*anti*aldoxime (BRADY and DUNN), 679.
$C_{12}H_{17}O_4N_3$ ω-Hydroxy-3:4-dimethoxy-*o*-tolylacetaldehydesemicarbazone (PERKIN), 956.

12 IV

$C_{12}H_{11}O_3N_2Br$ Citraconylbromotolylhydrazides (CHATTAWAY and HODGSON), 586.

12 VI

$C_{12}H_8O_2NCl_2BrS$ Benzenesulphonchlorobromophenylchloroamides (CHATTAWAY and CLEMO), 103.
$C_{12}H_9O_2NClBrS$ Benzenesulphonchlorobromoanilides (CHATTAWAY and CLEMO), 103.

C_{13} Group.

$C_{13}H_{10}$ Fluorene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

13 II

$C_{13}H_{10}O_3$ 2-Acetoxy-1-keto-4-methylene-1:4-dihydronaphthalene (DEAN and NIERENSTEIN), 594.
$C_{13}H_{11}N$ 2-Aminofluorene, additive compounds of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1351.
$C_{13}H_{12}O_4$ 1-Hydroxy-2-acetoxynaphthyl-4-carbinol (DEAN and NIERENSTEIN), 595.
$C_{13}H_{13}N$ Aminodiphenylmethane, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.
Tetrahydro-α-naphthaquinoline, additive compounds of trinitrobenzene and (SASTRY), 271.
$C_{13}H_{14}O_3$ 1:2-Dimethoxynaphthyl-4-carbinol (DEAN and NIERENSTEIN), 595.
$C_{13}H_{14}O_6$ Acetyl derivative of lactone $C_{11}H_{12}O_5$ (PERKIN), 972.

$C_{13}H_{14}N_2$ Diaminodiphenylmethane, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

13 III

$C_{13}H_2O_2Br_6$ Hexabromoxanthone (DHAR), 746.

$C_{13}H_4O_2Br_4$ Tetrabromoxanthone (DHAR), 745.

$C_{13}H_8O_4N_2$ α- and β-Nitroaminoxanthones (DHAR), 747.

$C_{13}H_9NS$ 1-Phenylbenzthiazole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.

$C_{13}H_{10}N_2Cl_2$ Benzaldehyde-3:5-dichlorophenylhydrazone (CHATTAWAY and ELLINGTON), 590.

$C_{13}H_{11}ON$ *p*-Aminobenzophenone, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

Substance, from pyrrole-2-aldehyde and acetophenone (LUBRZYNSKA), 1120.

$C_{13}H_{11}ON_5$ 3-Methyl-1:2:4-triazole-5-azo-β-naphthol (MORGAN and REILLY), 157.

$C_{13}H_{11}O_3N_3$ α-Benzoylamino-β-glyoxaline-4(or 5)-acrylic acid, and its salts (PYMAN), 194.

$C_{13}H_{13}O_2N$ Ethyl naphthylcarbamate, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{13}H_{13}O_3N_3$ Benzoyl-γ-histidine, and its salts (PYMAN), 195.

$C_{13}H_{17}O_5N$ *N*-Formyl-4:5-dimethoxy-2-β-methylaminoethylbenzoic acid, and its hydrochloride (PERKIN), 923.

$C_{13}H_{19}O_3N$ 4:5-Dimethoxy-2-β-dimethylaminoethylbenzaldehyde (PERKIN), 901.

13 IV

$C_{13}H_2O_6N_2Br_4$ Tetrabromodinitroxanthone (DHAR), 747.

$C_{13}H_4O_6N_2Br_2$ Dibromodinitroxanthone (DHAR), 747.

$C_{13}H_4O_8N_3Br$ Bromotrinitroxanthone (DHAR), 747.

$C_{12}H_5O_6N_2Br$ Bromodinitroxanthone (DHAR), 746.

$C_{13}H_8O_3N_2Cl_2$ Nitrobenzodichloroanilides (CHATTAWAY and CLEMO), 94.

$C_{13}H_8O_3N_2Br_2$ Nitrobenzodibromoanilides (CHATTAWAY and CLEMO), 94.

$C_{13}H_9O_2N_3Cl_2$ Nitrobenzaldehyde-3:5-dichlorophenylhydrazones (CHATTAWAY and ELLINGTON), 591.

$C_{13}H_9O_2N_3Br_2$ Nitrobenzaldehyde-3:5-dibromophenylhydrazones (CHATTAWAY and ELLINGTON), 591.

$C_{13}H_9O_3N_3Cl_2$ Nitrobenzoyl-3:5-dichlorophenylhydrazines (CHATTAWAY and ELLINGTON), 589.

$C_{13}H_9O_3N_3Br_2$ Nitrobenzoyl-3:5-dibromophenylhydrazines (CHATTAWAY and ELLINGTON), 589.

$C_{13}H_{10}ON_2Cl_2$ Benzoyl-3:5-dichlorophenylhydrazine (CHATTAWAY and ELLINGTON), 589.

Salicylaldehyde-3:5-dichlorophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{13}H_{10}ON_2Br_2$ Benzoyl-3:5-dibromophenylhydrazine (CHATTAWAY and ELLINGTON), 589.

Salicylaldehyde-3:5-dibromophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{13}H_{10}O_4N_2Br_2$ *p*-Nitrotoluene-*o*-sulphon-2:4-dibromoanilide (CHATTAWAY and CLEMO), 104.

13 V

$C_{13}H_8ON_2Cl_2Br_2$ Dichlorodibromodiphenylcarbamide (CHATTAWAY and CLEMO), 98.

$C_{13}H_{11}O_3NBr_2S$ *p*-Toluenesulphon-2:4-dibromoanilide (CHATTAWAY and CLEMO), 104.

$C_{13}H_9O_3N_2ClBr$ Nitrobenzochlorobromoanilides (CHATTAWAY and CLEMO), 94.

13 VI

$C_{13}H_9O_4N_2ClBr_2S$ *p*-Nitrotoluene-*o*-sulphon-2:4-dibromophenylchloroamide (CHATTAWAY and CLEMO), 104.

$C_{13}H_9O_4N_2Cl_3BrS$ *p*-Nitrotoluene-*o*-sulphonchlorobromophenylchloroamides (CHATTAWAY and CLEMO), 104.

$C_{13}H_{10}O_2NClBr_2S$ *p*-Toluenesulphon-2:4-dibromophenylchloroamide (CHATTAWAY and CLEMO), 104.

$C_{13}H_{10}O_2NCl_3BrS$ *p*-Toluenesulphonchlorobromophenylchloroamides (CHATTAWAY and CLEMO), 103.

$C_{13}H_{10}O_4N_2ClBrS$ *p*-Nitrotoluene-*o*-sulphonchlorobromoanilides (CHATTAWAY and CLEMO), 104.

$C_{12}H_{11}O_2NClBrS$ *p*-Toluenesulphonchlorobromoanilides (CHATTAWAY and CLEMO), 103.

C_{14} Group.

$C_{14}H_{10}$ Anthracene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

Phenanthrene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

Tolane, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

$C_{14}H_{12}$ Dihydroanthracene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

Stilbene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

$C_{14}H_{14}$ *s*-Diphenylethane, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

14 II

$C_{14}H_8O_5$ Trihydroxyphenanthraquinone (MUKHERJEE and WATSON), 622.

$C_{14}H_8Br_2$ Dibromoanthracene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

$C_{14}H_{10}O$ α- and β-Anthrols, additive compounds of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1354.

$C_{14}H_{10}O_2$ 5-Keto-2-methyl-4-methylene-βγ-indenopyran (1:4) (SASTRY and GHOSH), 178.

$C_{14}H_{11}N$ Aminophenanthrenes, additive compounds of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1350.

α- and β-Anthramines, additive compounds of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1353.

Methylacridine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{14}H_{12}O_2$ Benzyl benzoate, preparation of (BERKELEY), 520.

$C_{14}H_{15}N_3$ Dimethylaminoazobenzene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{14}H_{18}O_4$ Ethyl phenylsuccinates (WREN and WILLIAMS), 579.

$C_{14}H_{21}N$ 9-Aminoanthracene, additive compound with *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1353.

14 III

$C_{14}H_7O_6N$ Nitro-2:7-dihydroxyphenanthraquinone (MUKHERJEE and WATSON), 621.

$C_{14}H_8O_6S$ 2-Hydroxyphenanthraquinonesulphonic acid, barium salt (MUKHERJEE and WATSON), 620.

$C_{14}H_9O_4N$ Amino-2:7-dihydroxyphenanthraquinone (MUKHERJEE and WATSON), 621.

$C_{14}H_{11}O_2Cl$ 5-Keto-2:4-dimethyl-$\beta\gamma$-indenopyrylium chloride (SASTRY and GHOSH), 177.

$C_{14}H_{11}O_3N$ Carbanilino-oxybenzaldehydes (BRADY and DUNN), 675.

$C_{14}H_{12}ON_2$ 3-Acetylaminocarbazole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{14}H_{12}OCl_2$ Di-*o*-chlorobenzyl ether (LEONARD), 571.

$C_{14}H_{13}N_2Br$ Benzaldehydebromotolylhydrazones (CHATTAWAY and HODGSON), 584.

$C_{14}H_{11}O_3N_3$ Azoxyanisole, additive compound of trinitrobenzene and (SASTRY), 273.

$C_{14}H_{15}O_2N$ 4-Acetylamino-1-naphthyl ethyl ether, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{14}H_{16}O_2N_2$ *o*-Dianisidine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{14}H_{16}ClBi$ Di-*p*-tolylchlorobismuthine (CHALLENGER), 250.

$C_{14}H_{24}O_4N_2$ Dimethyl ethylenebis-β-amino-α-methylcrotonate (ROBINSON), 1045.

14 IV

$C_{14}H_5O_4NBr_2$ Dibromonitrophenanthraquinone (MUKHERJEE and WATSON), 623.

$C_{14}H_5O_6N_2Br$ Bromodinitrophenanthraquinone (MUKHERJEE and WATSON), 623.

$C_{14}H_6O_4NBr$ Bromonitrophenanthraquinones (MUKHERJEE and WATSON), 623.

$C_{14}H_7O_2NCl_2$ Phthalo-2:4-dichloroanil (CHATTAWAY and CLEMO), 97.

$C_{14}H_7O_2NBr_2$ Phthalo-2:4-dibromoanil (CHATTAWAY and CLEMO), 97.

$C_{14}H_8O_3N_2Br_4$ 2:4:2′:4′-Tetrabromo-oxanilide (CHATTAWAY and CLEMO), 101.

$C_{14}H_{10}O_5N_2S$ 2:7-Diaminophenanthraquinonesulphonic acid (+ H_2O) (MUKHERJEE and WATSON), 627.

$C_{14}H_{11}ONBr_2$ Phenylaceto-2:4-dibromoanilide (CHATTAWAY and CLEMO), 93.

$C_{14}H_{12}ON_2Cl_2$ Anisaldehyde-3:5-dichlorophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{14}H_{12}ON_2Br_2$ Anisaldehyde-3:5-dibromophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{14}H_{12}O_2N_3Br$ Nitrobenzaldehydebromotolylhydrazones (CHATTAWAY and HODGSON), 584.

$C_{14}H_{12}O_3N_3Br$ Nitrobenzoylbromotolylhydrazines (CHATTAWAY and HODGSON), 583.

$C_{14}H_{13}ON_2Br$ Benzoylbromotolylhydrazines (CHATTAWAY and HODGSON), 583.

Salicylaldehyde-5-bromo-*o*-tolylhydrazone (CHATTAWAY and HODGSON), 585.

$C_{14}H_{22}O_3NI$ 4:5-Dimethoxy-2-β-dimethylaminoethylbenzaldehyde methiodide (PERKIN), 903.

$C_{14}H_{23}O_3N_2I$ 4:5-Dimethoxy-2-β-dimethylaminoethylbenzaldoxime (PERKIN), 903.

14 V

$C_{14}H_7O_2NClBr$ Phthalochlorobromoanils (CHATTAWAY and CLEMO), 96.

$C_{14}H_8O_3N_2Cl_2Br_2$ Dichlorodibromo-oxanilides (CHATTAWAY and CLEMO), 100.

$C_{14}H_{11}ONClBr$ Phenylacetochlorobromoanilides (CHATTAWAY and CLEMO), 93.

C_{15} Group.

$C_{15}H_{10}O_2$ 3-Phenanthrol-4-aldehyde (SMITH), 569.

$C_{15}H_{10}O_2$ 8-Phenyl-γ-benzopyrone, and its platinichloride (WATSON), 305.

$C_{15}H_{10}O_4$ 7:8-Dihydroxy-3-phenyl-γ-benzopyrone (+ $2H_2O$) (GHOSH), 115.

$C_{15}H_{12}N_2$ 3:5-Diphenylpyrazole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{15}H_{14}O_4$ 2-Methoxy-1:4-ethylcarbonatomethylenenaphthalene (DEAN and NIERENSTEIN), 596.

15 III

$C_{15}H_{10}O_5N_2$ α- and β-Nitroacetylaminoxanthones (DHAR), 748.

$C_{15}H_{11}O_2N$ 4-Imino-7-hydroxy-2- and -3-phenyl-γ-benzopyrans, and their salts (GHOSH), 113.

$C_{15}H_{11}O_3N$ 4-Imino-7:8-dihydroxy-2- and -3-phenyl-γ-benzopyrans (+H_2O) (GHOSH), 114.

$C_{15}H_{11}O_3N_3$ 2-Phenyl-4-[1-acetylglyoxaline-4(or 5)-methylidene]-oxazolone (PYMAN), 193.

$C_{15}H_{12}N_2Cl_2$ Cinnamaldehyde-3:5-dichlorophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{15}H_{12}N_2Br_2$ Cinnamaldehyde-3:5-dibromophenylhydrazone (CHATTAWAY and ELLINGTON), 592.

$C_{15}H_{14}O_2N_2$ 5:6-Methylenedioxy-*o*-tolualdehydephenylhydrazone (PERKIN), 908.

$C_{15}H_{14}O_2I_2$ 3:3′-Di-iodo-4:4′-dimethoxydiphenylmethane (ROBINSON), 1087.

$C_{15}H_{14}O_6N_2$ Substance, from the action of nitric acid on cryptopine (PERKIN), 893.

$C_{15}H_{25}O_4Br$ Methyl menthyl bromosuccinates (COHEN, WOODROFFE, and ANDERSON), 229.

15 IV

$C_{15}H_{11}O_2N_2Br$ Phthalylbromotolylhydrazides (CHATTAWAY and HODGSON), 587.

$C_{15}H_{13}ON_2Br$ Anisaldehydebromotolylhydrazones (CHATTAWAY and HODGSON), 585.

15 V

$C_{15}H_{10}O_2N_2Cl_2Br_2$ Dichlorodibromomalonanilides (CHATTAWAY and CLEMO), 101.

C_{16} Group.

$C_{16}H_{10}O_4$ 8-Phenyl-γ-benzopyrone-2-carboxylic acid (WATSON), 305.

$C_{16}H_{12}O_3$ 7-Hydroxy-3-phenyl-5-methyl-γ-benzopyrone (+ $2H_2O$) (GHOSH), 117.

$C_{16}H_{12}O_5$ 2-Diphenylyloxyfumaric acid (WATSON), 304.

$C_{16}H_{14}O$ α- and β-Anthrol ethyl ethers, additive compounds of *s*-trinitrobenzene and (CADRE and SUDBOROUGH), 1354.

$C_{16}H_{18}N_2$ Diphenylpiperazine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{16}H_{19}N$ Benzylpropylaniline, and its picrate (SINGH), 791.

16 III

$C_{16}H_{11}O_2N_3$ 4-Nitronaphthalene-1-azophenol (SIRCAR), 772.

$C_{16}H_{13}O_2N$ 4-Imino-7-hydroxy-3-phenyl-5-methyl-γ-benzopyran (+ H_2O) (GHOSH), 116.

4-Imino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyran (+ $\frac{1}{2}H_2O$), and its salts (GHOSH), 109.

$C_{16}H_{13}O_3N$ 4-Imino-7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyran ($+\frac{1}{2}H_2O$) (GHOSH), 110.

$C_{16}H_{15}ON$ 5-Methyl-5:10-dihydroacridine, and its compound with *s*-trinitrobenzene (SASTRY), 272.

$C_{16}H_{15}O_2N$ Piperonylidene-β-phenylethylamine (HAMILTON and ROBINSON), 1033.

$C_{16}H_{15}O_3N_4$ *p*-Nitrobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol (SIRCAR), 773.

$C_{16}H_{15}N_2Br$ Cinnamaldehyde-3-bromotolylhydrazones (CHATTAWAY and HODGSON), 586.

$C_{16}H_{16}O_4N_2$ Carbanilino-3:4-dimethoxybenz*syn*aldoxime (BRADY and DUNN), 675.

$C_{16}H_{20}N_2S_2$ Dimethylaniline disulphide, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1348.

16 IV

$C_{16}H_{10}ON_2Br_2$ 2:4-Dibromobenzeneazo-β-naphthol, preparation of (CHATTAWAY and CLEMO), 105.

$C_{16}H_{15}ON_2Br$ *p*-Bromobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol (SIRCAR), 774.

$C_{16}H_{16}O_4N_2S$ *p*-Sulphobenzene-1-azo-1′:2′:3′:4′-tetrahydro-4-naphthol (SIRCAR), 773.

16 V

$C_{16}H_{10}ON_2ClBr$ Chlorobromobenzeneazo-β-naphthols (CHATTAWAY and CLEMO), 105.

C_{17} Group.

$C_{17}H_{12}O$ Phenyl α-naphthyl ketone, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{17}H_{14}O$ Phenyl cinnamylidenemethyl ketone, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{17}H_{14}O_2$ 3-Phenyl-2:7-dimethyl-2-benzopyrone (GHOSH), 112.

$C_{17}H_{14}O_3$ Phenyl 5:6-methylenedioxy-*o*-methylstyryl ketone (PERKIN), 910.

$C_{17}H_{16}O_4$ 3:4-Dimethoxyphenyl 2-hydroxystyryl ketone (HAMILTON and ROBINSON), 1037.

$C_{17}H_{17}N$ 1-Benzylidene-2-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (HAMILTON and ROBINSON), 1035.

17 III

$C_{17}H_{11}O_5N_3$ 4-Nitronaphthalene-1-azosalicylic acid (SIRCAR), 773.

$C_{17}H_{13}O_3N$ Acetyl derivative of 4-imino-7-hydroxy-3-phenyl-γ-benzopyran (GHOSH), 114.

$C_{17}H_{14}ON_2$ 1-Phenylbenzylidene-3-methyl-5-pyrazolone, additive compound of trinitrobenzene and (SASTRY), 273.

$C_{17}H_{15}ON$ 4-Imino-3-phenyl-2:7-dimethyl-γ-benzopyran, and its sulphate (GHOSH), 112.

$C_{17}H_{19}ON$ *N*-Phenylacetyl-*N*-methyl-β-phenylethylamine (HAMILTON and ROBINSON), 1034.

$C_{17}H_{19}O_3N$ Piperine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

17 IV

$C_{17}H_{15}O_3Cl_4Fe$ 3′:4′-Dimethoxy-2-phenyl-1:4-benzopyranol anhydroferrichloride (HAMILTON and ROBINSON), 1037.

C_{18} Group.

$C_{18}H_{12}$ Chrysene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

$C_{18}H_{18}$ Retene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

18 II

$C_{18}H_{12}O_5$ 3-Phenanthroxyfumaric acid (WATSON), 305.

$C_{18}H_{14}O_4$ Ethyl 8-phenyl-γ-benzopyrone-2-carboxylate (WATSON), 305.

$C_{18}H_{30}O_2$ Linolenic acid, oxidation of (SALWAY), 138.

18 III

$C_{18}H_{11}O_8N$ Nitro-2:7-diacetoxyphenanthraquinone (MUKHERJEE and WATSON), 621.

$C_{18}H_{11}ON_4$ 2:4-Bisbenzeneazophenol, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{18}H_{14}O_4N_2$ 2:7-Diacetylaminophenanthraquinone (MUKHERJEE and WATSON), 622.

$C_{18}H_{15}O_3N$ Acetyl derivative ($+\frac{1}{2}H_2O$) of 4-imino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyran (GHOSH), 110.

$C_{18}H_{16}ON_2$ Phenylhydrazone of 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene (DEAN and NIERENSTEIN), 595.

$C_{18}H_{21}O_7N$ Cryptopidic acid, and its salts (PERKIN), 894.

C_{19} Group.

$C_{19}H_{12}O_2$ 5-Keto-2-phenyl-4-methylene-βγ-indenopyran(1:4) (SASTRY and GHOSH), 179.

3-Phenyl-1:4-α-naphthapyrone ($+\frac{1}{2}H_2O$) (GHOSH), 116.

$C_{19}H_{12}O_3$ 4:5-Diketo-3-phenyl-2-methyl-βγ-indenopyran(1:4) (SASTRY and GHOSH), 180.

$C_{19}H_{13}N$ Phenylacridine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

$C_{19}H_{14}O$ Benzylidene derivative of 2-methoxy-1:4-methylenenaphthalene (DEAN and NIERENSTEIN), 596.

$C_{19}H_{14}O_6$ Acetyl derivative of 7:8-dihydroxy-3-phenyl-γ-benzopyrone (GHOSH), 115.

$C_{19}H_{19}N_3$ Paraleucaniline, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

19 III

$C_{19}H_{11}O_5N_3$ α-Nitroxanthoneazophenol (DHAR), 750.

$C_{19}H_{11}O_6N_3$ Phenyliminodinitroxanthone (DHAR), 749.

$C_{19}H_{13}ON$ 4-Imino-2- and -3-phenyl-1:4-α-naphthapyrans, and their salts (GHOSH), 121.

$C_{19}H_{13}O_2N$ 4-Amino-5-keto-3-phenyl-2-methyl-βγ-indenopyran(1:4) (SASTRY and GHOSH), 179.

$C_{19}H_{13}O_2Cl$ 5-Keto-2-phenyl-4-methyl-βγ-indenopyrylium chloride (SASTRY and GHOSH), 178.

$C_{19}H_{15}O_5N$ Acetyl derivative of 4-imino-7:8-dihydroxy-3-phenyl-γ-benzopyran (GHOSH), 115.

$C_{19}H_{17}O_2N_3$ Phenylhydrazone of 2-acetoxy-4-methylene-1:4-dihydronaphthalene (DEAN and NIERENSTEIN), 594.

19 IV

$C_{19}H_{14}O_2NCl$ 4-Amino-5-keto-3-phenyl-2-methyl-βγ-indenopyrylium chloride (SASTRY and GHOSH), 179.

C_{20} Group.

$C_{20}H_{10}O_{11}$ Flavogallone (BLEULER and PERKIN), 537.

$C_{20}H_{14}O_8$ Triacetoxyphenanthraquinone (MUKHERJEE and WATSON), 622.

$C_{20}H_{14}N_2$ *αα*-Azonaphthalene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{20}H_{16}N_2$ α-Aminoazonaphthylene, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

$C_{20}H_{18}O_5$ Anhydrocryptopidiol (PERKIN), 973.

$C_{20}H_{19}N$ Dibenzylaniline, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1346.

$C_{20}H_{20}O_4$ Cryptopidene (PERKIN), 926.

$C_{20}H_{20}O_5$ α- and *β-iso*Berberidol (PERKIN), 954.

α- and *β-iso*Cryptopidol (PERKIN), 947.

Ethyl 2-diphenylyloxyfumarate (WATSON), 304.

$C_{20}H_{20}O_6$ Cryptopidiol (PERKIN), 974.

20 III

$C_{20}H_{11}O_6N_3$ Dinitroanilinophenanthraquinone (MUKHERJEE and WATSON), 625.

$C_{20}H_{12}O_4N_2$ Nitroanilinophenanthraquinones (MUKHERJEE and WATSON), 624.

$C_{20}H_{13}O_3N_3$ *p*-Nitrobenzene-1-azo-4-anthrol (SIRCAR), 775.

$C_{20}H_{14}ON_2$ Benzene-1-azo-4-anthrol (SIRCAR), 775.

$C_{20}H_{15}ON$ 4-Imino-3-phenyl-2-methyl-1:4-α-naphthapyran ($+\frac{1}{2}H_2O$), and its sulphate (GHOSH), 111.

$C_{20}H_{15}O_3N$ *p*-Diphenylcarbamyloxybenzaldehyde (BRADY and DUNN), 676.

$C_{20}H_{15}O_6N$ Dehydronorketoanhydrocryptopic acid (PERKIN), 988.

$C_{20}H_{15}O_7N$ Acetylamino-2:7-diacetoxyphenanthraquinone (MUKHERJEE and WATSON), 622.

$C_{20}H_{16}O_3N_2$ *p*-Diphenylcarbamyloxybenzaldoxime (BRADY and DUNN), 676.

$C_{20}H_{17}O_4N$ Anhydroprotopine (PERKIN), 1025.

$C_{20}H_{17}O_5N$ Acetyl derivative of 4-imino-7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyran (GHOSH), 111.

$C_{20}H_{17}O_7N$ Norketoanhydrocryptopic acid (PERKIN), 988.

20 IV

$C_{20}H_{11}O_4N_2Br$ Bromo-*p*-nitroanilinophenanthraquinone (MUKHERJEE and WATSON), 625.

$C_{20}H_{12}O_7N_2S$ 2-Nitroanilinophenanthraquinonesulphonic acid (MUKHERJEE and WATSON), 625.

$C_{20}H_{13}ON_2Br$ *p*-Bromobenzene-1-azo-4-anthrol (SIRCAR), 775.

$C_{20}H_{14}O_4N_2S$ *p*-Sulphobenzene-1-azo-4-anthrol (SIRCAR), 776.

C_{21} Group.

$C_{21}H_{16}$ Di-α-naphthylmethane, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1344.

21 II

$C_{21}O_8O_{12}$ Flavogallol, and its salts (BLEULER and PERKIN), 533.

$C_{21}H_{10}O_{13}$ Flavogallonic acid (BLEULER and PERKIN), 536.

$C_{21}H_{14}O_6$ 7:8-Dihydroxy-2:3-diphenyl-γ-benzopyrone (GHOSH), 119.

$C_{21}H_{18}O_5$ 5:6:5′:6′-Di-methylenetetraoxydi-*o*-methylstyryl ketone (PERKIN), 909.

$C_{21}H_{16}O_{12}$ Gossipitrone (PERKIN), 153.
$C_{21}H_{24}Bi$ Tri-*p*-tolylbismuthine (CHALLENGER), 250.
$C_{21}H_{36}O_4$ Methyl menthyl camphorates (COHEN, WOODROFFE, and ANDERSON), 227.

21 III

$C_{21}H_{13}O_3N$ 2-Benzoylaminophenanthraquinone (MUKHERJEE and WATSON), 626.
$C_{21}H_{15}ON$ 3-Hydroxyphenanthrylideneaniline (SMITH), 570.
$C_{21}H_{15}O_2N$ 4-Imino-7-hydroxy-2:3 diphenyl-γ-benzopyran, and its hydrochloride (GHOSH), 117.
$C_{21}H_{15}O_3N$ 4-Imino-7:8-dihydroxy-2:3-diphenyl-γ-benzopyran $(+\frac{1}{2}H_2O)$ (GHOSH), 119.
$C_{21}H_{17}O_4N_3$ Dicarbanilino-oxybenzaldoximes (BRADY and DUNN), 677.
$C_{21}H_{18}O_4N_2$ Acetyl-*p*-diphenylcarbamyloxybenzaldoxime (BRADY and DUNN), 677.
$C_{21}H_{19}O_5N$ Ketoanhydrocryptopine (PERKIN), 986.
Keto*isoepi*cryptopirubin base, and its salts (PERKIN), 1018.
n- and *iso*-Protopines, and their salts (PERKIN), 1023.
$C_{21}H_{21}O_4N$ *n*- and *iso*-Anhydrocryptopines, and their salts)PERKIN), 975, 1002.
$C_{21}H_{21}O_5N$ Dehydro*epi*cryptopirubin hydroxide (PERKIN), 1017.
Hydroxyanhydrocryptopine, and its salts (PERKIN), 992.
Methylprotopines (PERKIN), 1027.
$C_{21}H_{21}O_6N$ Diketotetrahydroanhydrocryptopine (PERKIN), 998.
Base, from oxidation of anhydrocryptopine (PERKIN), 987.
$C_{21}H_{21}O_9N_3$ Dinitrocryptopines (PERKIN), 890.
$C_{21}H_{22}O_7N_2$ Nitrocryptopine (PERKIN), 893.
$C_{21}H_{23}O_2N_3$ Aminostrychnine, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.
$C_{21}H_{23}O_4N$ Anhydrodihydrocryptopines, and their salts (PERKIN), 937.
$C_{21}H_{23}O_5N$ *n*-, *iso*-, ψ-, and *epi*-Cryptopines, and their salts (PERKIN), 877, 984, 1008, 1014.
Hydroxy*iso*anhydrodihydrocryptopines, and their salts (PERKIN), 995.
$C_{21}H_{23}O_6N$ Dihydroxy*iso*anhydrodihydrocryptopine, and its platinichloride (PERKIN), 996.
$C_{21}H_{25}O_5N$ Dihydrocryptopines, and their salts (PERKIN), 931.
Hydroxytetrahydroanhydrocryptopine, and its platinichloride (PERKIN), 949.

C_{22} Group.

$C_{22}H_{17}N$ Triphenylpyrrole, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1347.

22 III

$C_{22}H_{15}O_3N$ Benzoyl derivative of 4-imino-7-hydroxy-3-phenyl-γ-benzopyran (GHOSH), 114.
$C_{22}H_{23}O_4N$ Methyl-ψ-anhydrocryptopine, and its hydriodide (PERKIN), 1006.
$C_{22}H_{23}O_5N$ Methoxyanhydrocryptopines (PERKIN), 991.
$C_{22}H_{23}O_4N$ *N*-Dimethyl*iso*tetrahydroberberine (PERKIN), 950.
Methyl*iso*anhydrodihydrocryptopine, and its salts (PERKIN), 945.
$C_{22}H_{25}O_5N$ Methylcryptopines, and their salts (PERKIN), 960, 999, 1019.
$C_{22}H_{26}O_5N_2$ Methylcryptopine(γ)oxime (PERKIN), 968.
$C_{22}H_{29}O_5N$ Tetrahydromethylcryptopine, and its salts (PERKIN), 896.

C_{23} Group.

$C_{23}H_{14}O_{13}$ Ethyl flavogallonate (BLEULER and PERKIN), 535.

$C_{23}H_{16}O_4$ 7-Acetoxy-2:3-diphenyl-γ-benzopyrone (GHOSH), 118.

23 III

$C_{23}H_{13}O_5N_3$ β-Nitroxanthoneazo-β-naphthol (DHAR), 749.

$C_{23}H_{13}O_6N_3$ β-Nitroxanthoneazo-1:5-dihydroxynaphthalene (DHAR), 749.

$C_{23}H_{17}O_3N$ Acetyl derivative of 4-imino-7-hydroxy-2:3-diphenyl-γ-benzopyran (GHOSH), 118.

Benzoyl derivative (+ $\frac{1}{2}H_2O$) of 4-imino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyran (GHOSH), 110.

$C_{23}H_{25}O_5N$ Ethoxyanhydrocryptopines (PERKIN), 991.

$C_{23}H_{25}O_6N$ Acetyl derivatives of *epi*cryptopines (PERKIN), 1010.

$C_{23}H_{28}O_5N_4$ Methylcryptopine(γ)semicarbazone (PERKIN), 969.

23 IV

$C_{23}H_{16}O_2N_2Br_2$ Dianilinodibromoxanthone (DHAR), 748.

$C_{23}H_{26}O_4NBr$ Ethyldihydro*iso*anhydrocryptopine bromide (PERKIN), 888.

$C_{23}H_{26}O_4NI$ Ethyldihydro*iso*anhydrocryptopine iodide (PERKIN), 888.

$C_{23}H_{29}O_6NS$ *N*-Methyl*iso*tetrahydroberberines, and their salts (PERKIN), 951.

C_{24} Group.

$C_{24}H_{21}N_3$ 1:3:5-Trianilinobenzene, additive compound of trinitrobenzene and (SASTRY), 272.

$C_{24}H_{20}O_5$ Quinhydrone, from 2-methoxy-1-keto-4-methylene-1:4-dihydronaphthalene and 1-hydroxy-2-methoxynaphthyl-4-carbinol (DEAN and NIERENSTEIN), 596.

24 III

$C_{24}H_{27}O_6N$ Acetylmethylcryptopine(γ) (PERKIN), 970.

24 IV

$C_{24}H_{33}O_4NS$ Anhydrotetrahydromethylcryptopine methosulphate (PERKIN), 926.

C_{25} Group.

$C_{25}H_{22}O_{13}$ Acetyl derivative of hexahydroxybenzophenone (BLEULER and PERKIN), 542.

C_{26} Group.

$C_{26}H_7O_4N_3$ Nitrodianilinophenanthraquinone (MUKHERJEE and WATSON), 625.

$C_{26}H_{16}O_4N_4$ Phenanthraquinone-2:7-bisazophenol (MUKHERJEE and WATSON), 628.

$C_{26}H_{18}O_2N_2$ Dianilinophenanthraquinones (MUKHERJEE and WATSON), 624.

26 IV

$C_{26}H_{18}O_5N_2S$ Dianilinophenanthraquinonesulphonic acid (MUKHERJEE and WATSON), 625.

C_{27} Group.

$C_{27}H_{46}O$ Cholesterol, constitution of, and its action with ozone (DORÉE and ORANGE), 46.

27 III

$C_{27}H_{13}O_{11}N$ Flavogallolanilide (BLEULER and PERKIN), 535.

$C_{27}H_{46}OS_3$ Cholesterol thio-ozonide (DORÉE and ORANGE), 52.

C_{28} Group.

$C_{28}H_{19}O_4$ α-Naphtholphthalein, additive compound of *s*-trinitrobenzene and (SUDBOROUGH), 1345.

28 III

$C_{28}H_{18}O_4N_2$ 2:7-Dibenzoyldiaminophenanthraquinone (MUKHERJEE and WATSON), 627.

$C_{28}H_{27}O_4N$ Anhydrotetrahydromethylcryptopine, and its salts (PERKIN), 899.

$C_{28}H_{27}O_6N$ Benzoyloxy*iso*anhydrodihydrocryptopine, and its hydrochloride (PERKIN), 997.

C_{29} Group.

$C_{29}H_{20}O_{13}N_6$(?) Substance from distyryl diketone and *s*-trinitrobenzene (SUDBOROUGH), 1346.

C_{30} Group.

$C_{30}H_{32}O_{15}$ Acid from acid $C_{31}H_{34}O_{15}$ and potassium hydroxide (BLEULER and PERKIN), 539.

30 III

$C_{30}H_{16}O_6N_2$ 2-Oxalylaminophenanthraquinone (MUKHERJEE and WATSON), 626.

$C_{30}H_{20}O_6N_4$ Phenanthraquinone-2:7-bisazophenyl acetate (MUKHERJEE and WATSON), 628.

C_{31} Group.

$C_{31}H_{34}O_{15}$ Acid, from methylation of flavogallol (BLEULER and PERKIN), 539.

C_{33} Group.

$C_{33}H_{20}O_{18}$ Acetylflavogallol BLEULER and PERKIN), 534.

$C_{33}H_{38}O_{15}$ Methyl ester of acid $C_{31}H_{34}O_{15}$ (BLEULER and PERKIN), 539.

33 III

$C_{33}H_{25}O_4N_3$ Diphenylcarbamyl-*p*-diphenylcarbamyloxybenzaldoxime (BRADY and DUNN), 678.

C_{34} Group.

$C_{34}H_{24}O_{18}$ Acetylflavogallone (BLEULER and PERKIN), 537.

34 III

$C_{34}H_{49}O_4N$ Cholesteryl nitrobenzoates (DORÉE and ORANGE), 54.

$C_{34}H_{50}O_2Br_2$ Cholesteryl benzoate dibromide (DORÉE and ORANGE), 54.

34 IV

$C_{34}H_{48}O_4NBr$ Bromocholesteryl *m*-nitrobenzoate (DORÉE and ORANGE), 54.

C_{36} Group.

$C_{36}H_{28}O_{20}$ Acetyl derivative of methyl flavogallonate (BLEULER and PERKIN), 536.

36 III

$C_{36}H_{20}O_6N$ 2-Phthalylaminophenanthraquinone (MUKHERJEE and WATSON), 626.

C_{37} Group.

$C_{37}H_{38}O_{20}$ Acetyl derivative of ethyl flavogallonate (BLEULER and PERKIN), 536.

C_{38} Group.

$C_{38}H_{28}O_2N_4$ Dibenzidinophenanthraquinone (MUKHERJEE and WATSON), 626.

C_{44} Group.

$C_{44}H_{24}O_8N_4$ 2:7-Diphthalyldiaminophenanthraquinone (MUKHERJEE and WATSON), 627.

C_{49} Group.

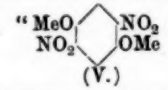
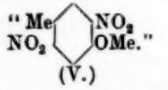
$C_{49}H_{36}O_2N_6$ Hexa-anilinoxanthone (DHAR), 748.

C_{63} Group.

$C_{63}H_{32}O_{18}$ Benzoylflavogallol (BLEULER and PERKIN), 535.

ERRATA.

VOL. CIX (TRANS., 1916).

Page	Line	
123	1*	*for* "silver" *read* "mercurous."
124	6*	,, "in" *read* "into."
125	17*	,, "water" *read* "ether."
127	9	,, "20·8" *read* "20·1."
127	5* col. i.	*for* "nitrite" *read* "nitrate."
130	6	,, "54·25" *read* "54·22."
131	4	
	15*	
	12*	
133	13*	*for* "nitromercaptides" *read* "mercury mercaptide nitrites."
134	16*	
	14*	
132	2	
133	12*	
	1*	
134	15*	,, "ethyl nitromercaptide" *read* "mercury ethylmercaptide nitrite."
136	1	
137	13	
134	15	
135	9	,, "methyl nitromercaptide" *read* "mercury methylmercaptide nitrite."
136	8	
137	15*	
583	4*	,, "m-*Nitrobenzoyl*-3-*bromo*-o-*tolylhydrazine*" read "m-*Nitrobenzoyl*-5-*bromo*-o-*tolylhydrazine*."
586	top	,, "*Cinnamaldehyde*-3-*bromo*-o-*tolylhydrazone*" read "*Cinnamaldehyde*-5-*bromo*-o-*tolylhydrazone*."
658	16	*for* "$CH_3 \cdot CH \| \| HO \cdot N$" *read* "$C_6H_5 \cdot CH \| \| HO \cdot N$"
662	7*	,, "$C_6H_5 \cdot CH \| \| Ac_2O \cdot N$" *read* "$C_6H_5 \cdot CH \| \| AcO \cdot N$."
694	20	,, "No HBr; temperature, 25·0° | No HBr; temperature, 40·4°," *read* "*N*/5HBr; temperature, 25·0° | *N*/5HBr; temperature, 40·4°."
823	2*	,, "$(MeO)_2C_6H_2 \cdot CHO$" *read* "$(MeO)_2C_6H_2Me \cdot CHO$."
1029	4*	,, "2893" *read* "2493."
1039	bottom	*for* "$NH_2 \cdot CMe{:}CHMe \cdot CO_2Et$" *read* "$NH_2 \cdot CMe{:}CMe \cdot CO_2Et$."
1079	9*	*for*  *read* 
1229		Table-Heading to cols 2 and 3, *delete* "small crystals."
		,, ,, ,, 6 and 7, ,, "90-mesh powder."
1343	9	*for* "substanced" *read* "substituted."

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Founded, 1841.

INCORPORATED BY ROYAL CHARTER, 1848.

CORRECTED TO AUGUST, 1916.

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LONDON, W.
1916.

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THE ORDINARY SCIENTIFIC MEETINGS for 1916-17 will be held on the following Thursdays at 8 p.m. :—

October	19th,†1916.	March	1st, 1917.
November	2nd, ,,	,,	15th* ,, Lecture by Dr. Horace T. Brown.
,,	16th,* ,,	April	19th,* ,,
December	7th, ,,	May	3rd, ,,
,,	21st,* ,,	,,	10th,† ,,
January	11th,†1917.	,,	17th,* ,, Lecture by Mr. A. Chaston Chapman.
,,	18th,* ,, Lecture by Col. C. T. Heycock	June	7th, ,,
February	1st, ,,	,,	21st,* ,,
,,	15th,* ,,		

*Council Meetings will be held on these days.

†Informal Meeting.

ANNUAL GENERAL MEETING, THURSDAY, MARCH 29TH, 1917, AT 4 P.M.

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THE CHEMICAL SOCIETY.

The Chemical Society was founded on February 23rd, 1841, and its first General Meeting was held on March 30th of that year. In 1848, a Charter of Incorporation was granted to the Society by the Crown, under the conditions of which it consists of Fellows, Honorary and Foreign Members, and Associates.* The Fellows elect out of their own body a Council consisting of a President, Vice-Presidents, a Treasurer, two Secretaries, a Foreign Secretary, and twelve other Fellows, by whom the business of the Society is conducted.

The object of the Society, as laid down in the Charter, is the general advancement of Chemical Science, by the discussion and publication of new discoveries, and the interchange of valuable information respecting them.

A Candidate for election as a Fellow of the Chemical Society must send to the Secretaries a Certificate subscribed by not less than five Fellows of the Society, to three at least of whom he must be personally known.† The Certificate will be read at three Ordinary Scientific Meetings of the Society, and a ballot for the election of the Candidate will afterwards be held. When elected, he will receive notice thereof from the Secretaries.

Each Fellow has the right to be present and to vote at all Meetings of the Society, and to propose Candidates for admission into the Society, and is entitled to one copy of the Annual Publications so long as his Annual Subscription be not in arrear. He is also entitled to the use of the books in the Society's Library, under such restrictions as the Council may deem necessary. He has the privilege of introducing to Ordinary Scientific Meetings of the Society, two visitors, whose names are entered in a book kept for that purpose, together with the name of the Fellow introducing such visitors.

When elected, every Candidate previous to admission is required, within three months from the date of his election, to pay an admission fee of £4, and either his first annual subscription, or his life composition fee; otherwise his election becomes void. The annual subscription to be paid by Fellows is £2. The subscriptions of Fellows become due on the first day of January of every year. The life composition fee is £30, excepting that Fellows who have paid ten annual subscriptions pay as life composition fee £20; Fellows who have paid fifteen annual subscriptions pay £15; Fellows who have paid twenty annual subscriptions pay £12; and Fellows who have paid twenty-five annual subscriptions pay £10.

If a Candidate be elected during the month of November or December, he will not be called upon to pay any annual subscription for

* No elections of Associates have taken place for many years.

† In the case of Candidates resident abroad unable to obtain this number of signatures, the Council have power to accept a certificate signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot.

the current year, and will not be entitled to receive the publications of the Society for that year.

Any Fellow who at the period of the Annual General Meeting of the Society in March owes two annual subscriptions, such subscriptions having been duly applied for, and no reason satisfactory to the President and Council having been assigned for their non-payment, shall cease to be a Fellow of the Society, and his name will be removed from the Society's List accordingly: Provided, nevertheless, that on a solicitation for re-admission being addressed to the President and Council by a person so circumstanced, the case of such person will be considered by the Council, who may, if they see fit, reinstate him as a Fellow of the Society, upon his paying the arrears of his subscription, or a life composition fee.

COMMUNICATION OF PAPERS.

The attention of Authors is directed to the following resolutions of Council regarding Scientific Communications submitted to the Chemical Society:

1. All Scientific Communications for the Transactions should be addressed to "The Secretaries, Chemical Society, Burlington House, W."

2. No title can be included in the list of Scientific Communications to be brought before any Ordinary Scientific Meeting of the Society unless the paper, or summary thereof, is received by the Secretaries on the Monday previous to the day of Meeting. The titles of Scientific Communications which are to be read cannot be announced in the *Morning Post* unless such Communications are received by the Secretaries at least three days before the Meeting.

3. Papers which are deemed by the Council unsuitable for publication in the Society's Transactions or which have been withdrawn for publication by the Author shall be deposited in the Society's Archives. Authors are therefore advised to retain copies of their papers.

4. All papers communicated to the Society, with their illustrative drawings, shall become the property of the Society, unless stipulation be made to the contrary, and Authors shall not be at liberty, save by permission of the Council, to publish elsewhere the papers they have communicated until such papers have appeared in the Transactions of the Society, or have been returned to the Author, or withdrawn from publication by the Author. Communications which have appeared in any other Journal shall not be published in the Society's Transactions unless this course is approved by a special vote of the Council.

5. The address to which proofs are to be sent should be written on every paper.

6. If Authors require more than the 50 reprints allowed by the Society, they should inform the Editor at the time they send in their

corrected proofs, when the extra copies will be supplied at rates which can be obtained from the Printers.

7. Illustrations for the Transactions (including curves) are, as far as possible, executed in photographic "process" work, and, accordingly, drawings, etc., accompanying the papers must be carefully drawn, about twice the size of the finished block, on smooth, white Bristol board in Indian ink, so as to admit of the blocks being prepared directly from the drawings. Any lettering on these drawings should be of such a size that it will be clearly legible when reduced. When it is necessary to use plates, these must be also of convenient dimensions.

PUBLICATIONS OF THE SOCIETY.

With the exception of certain numbers of the Journals and Proceedings which are out of print, the following publications may be obtained from Messrs. Gurney and Jackson, 33, Paternoster Row, E.C.:

	Price to Fellows. £	s.	d.	Price to Public. £	s.	d.
Memoirs and Proceedings, 1841-1847 (3 Vols.) ... per vol.	1	0	0	1	10	0
Quarterly Journal, 1848-1862 (14 Vols.)... ... ... per vol.	1	0	0	1	10	0
,, ,, ,, ,, (Single Parts) ... ... per part		5	0		7	6
Journal, 1862-1895 ... ... per ann.	1	10	0	1	10	0
,, ,, ,, (Single Parts) ... ... per part		2	6		2	6
,, 1896-1914 ... ... per ann.	2	0	0	2	0	0
,, ,, ,, (Single Parts) ... ... per part		3	6		3	6
Journal and Proceedings, 1915 (onwards) ... ... per ann.	3	0	0	3	0	0
,, ,, ,, ,, ,, (Single Parts) per part		5	0		5	0
*Proceedings, 1885-1914 ... ... per vol.		7	6		7	6
,, ,, (Single Parts) ... ... per part			6			6
Annual Reports on the Progress of Chemistry (bound in cloth), Vol. I (1904) to present date ... ... per vol.		4	6		4	6
Collective Index, Vol. I. 1841-1872 ... ... per vol.		4	0		4	0
† ,, ,, ,, II. 1873-1882 .. .. per vol.		10	0		15	0
† ,, ,, ,, III. 1883-1892 ... ... per vol.		15	0	1	0	0
† ,, ,, ,, IV. 1893-1902 ... ... per vol.	1	0	0	1	10	0
‡ ,, ,, ,, V. 1903-1912 ... . per vol.	2	0	0	2	10	0
‡Jubilee Volume (giving history of the Chemical Society from 1841-1891)		2	6		2	6
‡Memorial Lectures, 1893-1900 (Out of print)		7	6		7	6
,, ,, Vol. II. 1901-1913		6	0		6	0
‡Library Catalogue, 1886		1	0		1	0
‡ ,, ,, 1903		2	6		2	6
‡Cases for binding the Journal in 4 vols. ... ... per ann.		4	0		4	0

Tables of International Atomic Weights for 1917 (as recommended by the International Atomic Weights Committee):

ON CARDS: 1*s.* per dozen; 4*s.* for 50; 7*s.* 6*d.* per 100. Postage extra.

ON PAPER: 4*d.* per dozen; 1*s.* for 50; 1*s.* 9*d* per 100. Postage extra. (*Suitable for pasting into Note Books.*)

* Included with Journal as from January, 1915.
† Postage to Fellows One Shilling extra. ‡ Post free to Fellows.

The *Journal*, which is published on the last day of each month, includes the Proceedings, papers communicated to the Society and Abstracts of chemical papers published in other Journals.

The *Annual Reports on the Progress of Chemistry* contain an epitome of the principal definite steps in advance which have been made during the year. Fellows can obtain, from the Assistant Secretary, cases for binding the Annual Reports, price One Shilling each.

RESEARCH FUND.

The Research Fund of the Chemical Society has been established for the purpose of assisting investigators by defraying the cost of expensive materials. The income accruing from the munificent donations received from the Goldsmiths' Company and from the Perkin Memorial Fund will be devoted as far as possible to the encouragement of research in (*a*) metallurgical and inorganic chemistry and (*b*) the chemistry of coal-tar products, respectively.

The Committee meets twice a year to consider applications for grants; and forms of application, which can be obtained from the Assistant Secretary, must be lodged with the Secretaries by the end of May and November in each year.

LIBRARY RULES.

1. The Library is open for reference, and for the issue and return of books, daily from 10 a.m. to 6 p.m. (Saturdays 10 a.m. to 1 p.m.); and in the evenings of those days on which the Chemical Society meets.

2. Fellows are not allowed to have on loan more than *six* volumes at a time, without special permission from the Librarian.

3. All Journals, Dictionaries, and Pamphlets of which there are not duplicate copies, and certain early Chemical and other Books distinguished in the Library Catalogue by a star, belong to the Reference Library, and are not for general circulation. Fellows desiring to borrow books from the Reference Library must make a special application in writing to the Librarian, undertaking to bear all risks of transit, &c., and to return the volumes within one month; the Librarian may then, at his discretion, issue such books. This regulation does not apply, however, to volumes of Periodicals of which no duplicate copies exist in the Library.

4. A book may not be taken out of the Library until one month after it has been received.

5. Books must not be removed from the Library until a voucher for them has been signed and delivered to the Librarian.

6. Books are issued either to the Fellow desiring the loan, or to a person bringing a written order from him. In either case a receipt must be given on the form provided. When a Fellow desires a book or books to be sent to him, he must send to the Librarian a written order, and pay the whole cost of carriage. All books borrowed by Fellows shall be at the risk of the borrower from the moment they are issued or despatched by the Librarian, and until they are returned to him.

7. Books may not be sent out of the United Kingdom.

8. Books which have been bespoken shall circulate in the order of application.

9. Fellows shall be at liberty to retain a book one calendar month, unless, at the expiration of a fortnight, notice is received that the book is required by another Fellow, in which case it must be returned at once. Single parts of journals may not be retained longer than one week.

10. The names of Fellows borrowing books shall be entered by the Librarian, or Officer in attendance, in a book kept for that purpose. When a Fellow returns a book, his voucher shall be given to him, and a record of the return duly made.

11. In the case of Fellows returning books by messenger or public conveyance, the voucher shall be returned by the Librarian through the post.

12. Fellows retaining books longer than the time specified, or neglecting to return them when demanded, shall forfeit the right to borrow books from the Library until the volume or volumes be returned.

13. Fellows to whom books have been issued shall be held responsible for their preservation from injury; and if any book when returned is found to have been damaged, the Council may order that it be repaired or replaced at the expense of the borrower. In the event of any book being lost, or being detained after application has been made for its return, the Council may replace, at the cost of the borrower, the volume or volumes so lost or detained. This rule shall also apply to single parts of current periodicals.

14. For the purpose of revision and cleaning, the Library shall be closed for a fortnight in August of each year; before which time all books must be returned, unless special permission has been previously obtained from the Librarian. In the event of any book not being returned on such occasion, the Council may replace it at the cost of the borrower.

15. No persons other than Fellows of the Society have the privilege of using the Library, except upon a written introduction from a Fellow, with whom rests the responsibility for all books consulted by the person introduced. Such introduction shall be valid for one occasion only.

FORM TO BE USED FOR NOTIFYING CHANGE OF ADDRESS.

Name
(*in full*)

Present Address

Degrees
(*with names of Universities*)

Previous Address

Remarks

THE ASSISTANT SECRETARY,
CHEMICAL SOCIETY,
BURLINGTON HOUSE, PICCADILLY, W.

NAMES OF HONORARY AND FOREIGN MEMBERS.

NUMBER NOT TO EXCEED FORTY.

Date of Election.	
Jan. 20, 1898	*Arrhenius, Prof. Dr. Svante August, F.R.S., Bergsgaten 18, Stockholm
March 2, 1911	Ciamician, Prof. Giacomo, Regia Universita, Bologna, Italy
May 18, 1904	Clarke, Prof. Frank Wigglesworth, LL.D. (Aberd.), United States Geological Survey, Washington, D.C., U.S.A.
May 18, 1904	Curie, Madame Marie, La Sorbonne, Paris
Jan. 20, 1898	Franchimont, Prof. Dr. Antoine Paul Nicolas, Rapenburg 104, Leyden
Feb. 6, 1908	Gautier, Prof. Armand Emile Justin, 9, Place-des-Vosges, Paris
March 7, 1912	Guye, Prof. Philippe Auguste, D.Sc. (Geneva and Paris), 3, Chemin Bizot, Geneva, Switzerland
Feb. 6, 1908	Haller, Prof. Albin, 10, Rue-Vauquelin, Paris
Jan. 20, 1898	Körner, Prof. Guglielmo, R. Scuola Superiore d'Agricoltura, Milan
June 5, 1913	Konovaloff, Geh. Rat. Prof. Dmitri Petrovitsch, Ministergehilfe für Handel und Industrie, Petrograd, Russia
Feb. 6, 1908	Le Bel, Joseph Achille, F.R.S., 250, Rue Saint Jacques, Paris
Feb. 6, 1908	Le Chatelier, Prof. Henri Louis, 73, Rue Notre Dame des Champs, Paris
March 4, 1909	Lunge, Georg, Prof., Ph.D. (Breslau), Hon. Dr. Ing. (Karlsruhe), Carmenstrasse 37, Zürich, Switzerland
May 18, 1904	Morley, Prof. Edward Williams, Hon. D.Sc. (Yale), West Hartford, Conn., U.S.A.
March 7, 1912	Osborne, Dr. Thomas Burr, 52, Trumbull-street, Newhaven, Conn. U.S.A.
Jan. 20, 1898	Remsen, Prof. Ira, Johns Hopkins University, Baltimore, U.S.A.
Feb. 6, 1908	†Richards, Prof. Theodore William, S.B. and Hon. LL.D. (Haverford), A.M., Ph.D. (Harvard and Christiania), Hon. D.Sc. (Harvard, Oxon. and Manc.), Hon. Sc.D. (Yale), Hon. Ph.D. (Prague), Hon. Chem. D. (Clark Univ.), Hon. M.D. (Berlin), Hon. D.Sc. (Cantab.), Harvard University, Cambridge, Mass., U.S.A.
June 16, 1892	Schlœsing, Prof. Dr. Théophile, Institut Agronomique, Paris

† Faraday Lecturer, 1911. * Faraday Lecturer, 1914.

Date of Election.	
Jan. 20, 1898	Waals, Prof. Dr. Johannes Diderik van der, P.C., Hooftstraat 117, Amsterdam
March 7, 1912	Walden, Prof. Paul, Mem. Imp. Russ. Acad. Sc. (Petrograd), Ph.D. (Leipzig), M.Chem. (Odessa), D.Chem. (Petrograd), The Polytechnik, Riga, Russia
June 5 1913	Werner, Prof. Alfred, Freie-strasse 111, Zürich, Switzerland

FARADAY LECTURERS.

1869. Jean Baptiste André Dumas.
1872. Stanislao Cannizzaro.
1875. August Wilhelm von Hofmann.
1879. Charles Adolphe Wurtz.
1881. Hermann Ludwig Ferdinand von Helmholtz.
1889. Dmitri Ivanovitsch Mendeléeff.
1895. John William Strutt, Lord Rayleigh.
1904. Wilhelm Ostwald.
1907. Emil Fischer.
1911. Theodore William Richards.
1914. Svante August Arrhenius.

LONGSTAFF MEDALLISTS.

1881. Thomas Edward Thorpe.
1884. Cornelius O'Sullivan.
1888. William Henry Perkin.
1891. Francis Robert Japp.
1894. Horace Tabberer Brown.
1897. William Ramsay.
1900. William Henry Perkin, jun.
1903. William Jackson Pope.
1906. Walter Noel Hartley.
1909. Frederic Stanley Kipping.
1912. Herbert Brereton Baker.
1915. Martin Onslow Forster.

In order that the List of Fellows may be as complete as possible, those Fellows whose names and degrees do not appear in full are requested to communicate with the Assistant Secretary. Inaccuracies and changes of Address should be reported without delay on the form attached.

NAMES OF FELLOWS.

‖ Denotes Life Members.
Trans. Denotes Fellows who have contributed Papers published in the Society's Transactions.
Proc. " " " " " " " " Proceedings.
C. " " " served on Council of the Society; P. as President; V.P. as Vice-President; T. as Treasurer; S. as Secretary; F.S. as Foreign Secretary.

Date of Election.			
1903	Trans.		Abell, Robert Duncombe, D.Sc. (Wales), Ph.D. (Leipzig), F.I.C., University College of South Wales and Monmouthshire, Cardiff
1871	Trans.	C. 1882-4	Abney, Sir William de Wiveleslie, K.C.B., Hon. D.C.L. (Dun.), Hon. D.Sc. (Vict.), Sc.D. (Dub.), F.R.S., F.I.C., Rathmore Lodge, Bolton-gardens-south, S.W.
1883			Abraham, Alfred Clay, F.I.C., 87, Bold-street, Liverpool
1913			Acland, Theodore William Gull, B.A. (Cantab.), King's College, Cambridge, and 19, Bryanston-square, W.C.
1875	Trans.		Acworth, Joseph John, Ph.D. (Erlangen), F.I.C., Thornbank, Shootup-hill, Brondesbury, N.W.
1913			Adam, Neil Kensington, B.A. (Cantab.), Kingsnorth Air Station, Hoo, Rochester.
1892			‖Adams, Arthur, F.I.C., 66, Edgbaston-road, Smethwick
1915			Adams, Basil Albert, 118, High-street, Beckenham
1910			Adams, Percival Frederick, 81, Rock-avenue, Gillingham, Kent
1892			Adcock, Samuel Robert, The St. Helens Smelting Co., Atlas-court, St. Helens
1896			Addie, Robert, Suffolk House, Laurence Pountney Hill, E.C.
1881	Trans.		Adeney, Walter Ernest, Hon. D.Sc. (R.U.I.), A.R.C.S.I., F.I.C., Burnham, Queen's-park, Monkstown, Co. Dublin
1885	Trans.		Adie, Richard Haliburton, M.A. (Cantab.), B.Sc. (Lond.), 136, Huntingdon-road, Cambridge
1909	Trans.		Adlam, George Henry Joseph, B.A. and B.Sc. (Oxon.), City of London School, Victoria Embankment, E.C.
1885			Adriance, John Sabine, Ph.D., Williams College, Williamstown, Mass, U.S.A.

Date of Election		
1913		Advani, Parmanand Mewaram, M.A. and B.Sc. (Bombay), Dayaram Jethmal Sind College, Karachi, India
1916	Trans.	Agashe, Ganesh Sakharan, Prof., M.A. (Bombay), M.Sc. (Manc.), Theosophical Society, Adyar, Madras, S. India.
1914		Ahmad, Abdel Hameed, B.Sc. (Birm.), 16, Saieda Aisha-street, Khalifa, Cairo, Egypt
1908	Proc.	Akers, Noel Charles, F.I.C., 16, Avenue Mansions, Hampstead, N.W.
1879		Albright, George Stacey, M.A. (Cantab.), Bromesberrow-place, Ledbury
1893		Albuquerque, John Pedrozo d', Prof., M.A. (Cantab.), F.I.C., Government Laboratory, Barbados, West Indies
1892		Alcock, John While, 44, Princess-road, Edgbaston, Birmingham
1916		Alder, George Arthur, 45, Lothian-road, Middlesbrough
1903		Alderton, Gilbert John, B.Sc. (Lond.), F.I.C., 68, Dunvegan-road, Eltham, S.E.
1914		Allan, Hugh Logie, c/o The Burma Oil Co., Ltd., P.O. Box 67, Rangoon, Burma
1886		Allan, James Henry, L.R.C.P. and L.R.C.S. (Edin.), 47, St. Domingo-grove, Everton, Liverpool
1896		Allan, John, 77, Northern-grove, West Didsbury, Manchester
1907		Allan, John Campbell, Iona-terrace, Helensburgh
1912		Allcock, Thomas, Glan Usk, The-avenue, Marton, Yorkshire
1907		Allen, Alfred Frederick, B.Sc. (Lond.), 35, Purrett-road, Plumstead, S.E.
1894		Allen, Frederick John, Phœnix Chemical Works, Upper North-street, Poplar, E.
1870		Allen, John, Phœnix Chemical Works, Upper North-street, Poplar, E.
1904		Allen, William Harold Richard, c/o Straits Trading Co., Butterworth, Penang, Straits Settlements
1894		Allibon, George Henry, 23, Deramore-park, Belfast
1905		Allison, James Albert, Luchana Laboratory, Apartado 45, Bilbao, Spain
1908	Trans.	Allmand, Arthur John, D.Sc. (L'pool), Muspratt Laboratory, The University, Liverpool
1899		Allworthy, James Herbert, B.Sc. (Lond.), Northaldin, Lower Addiscombe-road, Addiscombe, Croydon
1899		Allworthy, Samuel William, M.A., M.D., D.P.H. (Dub.), The Manor House, Antrim-road, Belfast
1915		Alpe, Frank Theodore, Bracondale, Wymondham, Norfolk
1903		Alton, William Lester St. John, F.I.C., The Radium Institute, 16, Riding House-street, Portland-place, W.

Date of Election.		
1912		Amies, Edwin John, B.Sc. (Lond.), A.R.C.S., 10, Salisbury-road, Thorpe Hamlet, Norwich
1885	Proc.	‖Amphlett, Edward Greenhill, M.A. (Oxon.), 3, Union-place, Worthing
1915		Anderson, Alfred, Hamer House, Egerton, Bolton.
1911		Anderson, Edward, Hill View House, Waun Wen-road, Swansea
1895		Anderson, Herbert, The Blue School, Wells
1899		Anderson, James William, Cliffe Lodge, Cliffe-at-Hoo, Rochester
1901	Trans.	Anderson, William Carrick, M.A., D.Sc. (Glas.), 7, Scott-street, Garnethill, Glasgow
1892		‖Anderson, William Smellie, The Royal Mint, Ottawa, Ontario, Canada
1908		Andreae, Edward Philip, Ph.D. (Berlin), c/o The British Glanzstoff Manufacturing Co., Ltd., Flint
1905	Trans.	Andrews, Albert Edward, St. Hilda, 20, Carew-road, Thornton Heath, Surrey
1888		Andrews, Edward Arthur, St. Mary's Hospital, Paddington, W.
1882		‖Andrews, Launcelot Winchester, M.A. and Ph.D. (Göttingen), Ph.B. (Yale), 6643, Stewart-avenue, Chicago, Ill., U.S.A.
1915		Andrews, William Arthur, B.Sc. (Birm.), 22, The Avenue, Carmarthen
1914		Anfilogoff, Nicholas Alexander, c/o The London and Thames Haven Oil Wharves, Ltd., Thames Haven, Essex
1905	Trans.	Angel, Andrea, M.A. and B.Sc. (Oxon.), c/o Messrs. Brunner Mond and Co., Crescent Wharf, Silvertown, E.
1877		Angell, John, F.I.C., 6, Beacon's-field, Derby-road, Withington, Manchester
1909		Anklesaria, Jehangir Dhanjishaw, 9, Dalhousie-square, Calcutta, India
1909		Annett, Harold Edward, B.Sc. (Lond.), F.I.C., Indian Agricultural Service, Dacca, Bengal, India
1905		‖Anthony, Charles, jun., F.R.S.E., M.Inst. C.E., Casilla de Correo, 149, Bahia Blanca, Argentine, S. America
1910	Trans.	Applebey, Malcolm Percival, M.A. and B.Sc. (Oxon.), Leyden House, Mortlake, S.W.
1879		‖Appleby, Herbert, Ivydene, Kenwood-road, Stretford, Manchester
1903		Appleyard, George Henry, F.I.C., 1, Carlton-terrace, Hornsea, Hull
1890	Trans.	Appleyard, James Robert, Royal Technical Institute, Salford
1903		‖Appleyard, Percy, Albany, Western Australia
1884		Archbutt, Leonard, F.I.C., The Yews, Madeley-street, Derby
1912		Arkell, Daniel, B.Sc. (Lond.), The Oratory, Hagley-road, Birmingham
1875		Armistead, William, M.B. and C.M. (Edin.), Stapleford, Cambridge

Date of Election.			
1915			Armitage, Frederick Louis, Clinical Laboratory, Gleeson's Buildings, Auckland, New Zealand
1914			Armstrong, Charles Frank, Marhourah Sugar Works, Marhourah, Saran, Behar, India
1903	Trans.		‖Armstrong, Edward Frankland, D.Sc. (Lond.), Ph.D. (Berlin), F.C.G.I., c/o Messrs. J. Crosfield & Sons, Ltd., Bank Quay Works, Warrington
1899			Armstrong, Frederick William, 1, Palewell-park, East Sheen, S.W.
1870	Trans.	C. 1873-5; S. 1875-93; P. 1893-5	‖Armstrong, Henry Edward, Prof., LL.D. (St. Andrews), Ph.D. (Lips.), F.R.S., 55, Granville-park, Lewisham, S.E.; and Central Technical College, Exhibition-road, S.W.
1909			Armstrong, James Alexander Haddon, c/o Messrs. Romer Robinson & Co., Field-street-buildings, Durban, Natal, S. Africa.
1905			Arnaud, Francis William Frederick, F.I.C., County Analyst's Laboratory, Sessions House, Maidstone
1909			Arnfield, Harold, Peak Lodge, Buxton-road, Stockport
1906	Trans.		Arup, Paul Seidelin, M.A. (Nova Scotia), B.Sc. (Lond.), A.I.C., c/o The Aylesbury Dairy Co., Ltd., 31, St. Petersburg-place, Bayswater, W.
1899	Trans.		‖Ashcroft, Frederick Noel, M.A. (Oxon.), 37, Palace-court, Bayswater, W.
1903			Ashdown, Herbert Henry, 119, Herbert-road, Woolwich, S.E.
1911			Ashe, Albert, 55, Warrior-square, Southend-on-Sea
1913			Askew, Richard Watson, B.A. (Cape of Good Hope), Victoria College, Stellenbosch, Cape Colony, S. Africa
1901			Aspinall, Thomas, 34, Chorley New-road, Bolton
1900	Trans.		Aston, Bernard Cracroft, F.I.C., 71, Devon-street, Wellington, New Zealand
1901	Trans.		Aston, William George, The Square, Valentines-park, Ilford, E.
1911			Atkins, Ernest Andrew, 71, East-hill, Wandsworth, S.W.
1903			Atkinson, Edwin Bayles, 24, Dock-street, Hull
1903	Trans.		Atkinson, Harford Montgomery, B.Sc. (Wales), Ph.D. (Göttingen), Municipal Technical Institute, Limerick, Ireland
1911			Atkinson, Norman Ernest, 22, Ellesmere-road, Stockton Heath, Warrington
1916			Atkinson, Ralph Hall, B.A. (Cantab.), West Shaws, Barnard Castle
1872	Trans.		‖Atkinson, Robert William, B.Sc. (Lond.), F.I.C., 10, North Church-street, Cardiff
1914			Atlas, Henry, 58, High-street, Dartford
1903	Trans.		Attwell, Herbert Moore, A.R.C.S., 47, Beech Croft-road, Oxford
1908			Aubertin, Thomas, B.A. (Oxon.), Aboukir Lodge, Carnoustie, Forfarshire
1903			Aubrey, Henry James, The Cross, Worcester

Date of Election		
1910		Auchinleck, Gilbert Grahame, B.Sc. (McGill), Board of Agriculture, Réduit, Mauritius
1895	Trans.	‖Auden, Harold Allden, 13, Broughton-drive, Grassendale, Liverpool
1886		‖Audley, James Aloysius, B.Sc. (Lond.), A.R.C.S., F.I.C., 17, Gladstone-place, Hanley
1911	Trans.	Auld, Samuel James Manson, D.Sc. (Lond.), Ph.D. (Würzburg), F.I.C., Brackenhurst, Wokingham-road, and University College, Reading
1915		Aumonier, Frederic Sutcliffe, B.Sc. (Lond.), F.I.C., Rousdon Cottage, Bushey Heath, Watford
1906	Trans.	‖Austin, Percy Corlett, M.A. (Cantab.), D.Sc. (N.U.I.), 24, Kiln-lane, St. Helens
1892		‖Avery, David, M.Sc. (Melbourne), 387, Barkers-road, Kew, Melbourne, Australia
1896		Aykroyd, Henry Edward, Woodbank, Harden, Bingley
1908		Ba, Maung, B.A. (Calcutta), Rangoon College, Rangoon, Burma.
1915		Bacharach, Alfred Louis, B.A. (Cantab), 7, Strathray-gardens, Eton-avenue, N.W.
1912	Trans.	‖Backer, Hilmar Johannes, D.Chem. (Leyden), 20, Zuiderpark, Groningen, Holland
1914		Bacon, Raymond Foss, Prof. A.M., B.Sc., Ph.D. (Chicago), Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., U.S.A.
1914	Trans.	Bacon, William, B.Sc. (Lond.), F.I.C., Springfield, Springfield-road, New Southgate, N.
1913		Badami, Sankar Rao Bheemaji, M.A. (Madras), Badami House, Hulsurpet, Bangalore, India
1903		‖Badcock, William Cornish, M.A. (Cantab.), Northampton and County School, Northampton
1907	Trans.	Bagley, George, c/o Young's Chemical Works, 14, Egmont-street, Wellington, New Zealand
1913		Bailey, Alan Milsom, F.I.C., c/o The National Explosives Co., Ltd., Hayle, Cornwall
1912	Trans.	Bailey, Clement William, M.Sc. (Birm.), Evington, Leicester
1907		Bailey, Francis James, Roscrea, Findon Hill, Sacriston, Durham
1875	Trans.	‖Bailey, George Herbert, Ph.D. (Heidelberg), D.Sc. (Lond.), The University, Manchester; and Edenmor, Kinlochleven, Argyll
1893		Bailey, Henry, Belmont, Grosvenor-road, West Wickham, Kent
1912		Bailey, William Llewelyn, Central Buildings, Matlock Bank, Matlock
1900	Trans.	Bain, Alexander William, B.A. and B.Sc. (Lond.), F.I.C., Fairlight, Muswell-rise, Muswell Hill, N.

Date of Election.			
1891			Bairstow, John, Burley, Queen's-park, Chester
1901			Baker, Arthur, Denehurst, Earnsdale, Darwen
1889			‖Baker, Charles Frederic, B.Sc. (Lond.), Ph.D. (Strassburg), Technical College, and 29, Roker-park-road, Sunderland
1883	Trans.		‖Baker, Charles John, The Schools, Shrewsbury
1899			Baker, Clement Harrison, c/o Messrs. C. Harrold & Co., 2 and 3, St. Paul's-square, Birmingham
1902			Baker, Frederick Guy Stirling, M.A. (Oxon.), F.I.C., Marryatt's Lodge, Snaresbrook, Essex
1881	Trans.		Baker, Harry, F.I.C., Epworth House, Moughland-lane, Runcorn
1884	Trans.	C. 1899-03 V.P. 1913-16	†‖Baker, Herbert Brereton, Prof., M.A. and D.Sc. (Oxon.), F.R.S., Imperial College of Science and Technology, S. Kensington, S.W.; and Latchmoor House, Gerrard's Cross, Bucks.
1893	Trans.	C. 1908-11	Baker, Julian Levett, F.I.C., Ardingly, Linden-avenue, Maidenhead
1908	Proc.		Baker, Thomas James, D.Sc. (Lond.), B.Sc. (Birm.), St. Margaret's Lodge, Chester-road, Erdington, Birmingham
1901			Baker, Thomas Thorne, Farleigh Lodge, Warham-road, S. Croydon
1915			Ball, Frederick Charles, 479, Reddings Lane, Hall Green, Birmingham
1901	Trans.		Ball, Walter Craven, M.A. (Oxon.), Sc.D. (Dub.), F.I.C., c/o Sanitary Officer, Boulogne Base, B.E.F., France
1892			‖Ballantyne, Horatio, F.I.C., 75, Chancery-lane, W.C.
1908			Ballantyne, William Henry, B.Sc. (Glas.), Vine Cottage, Sevenoaks
1896			Ballingall, William, M.A. (St. Andrews), 9, Dudhope-terrace, Dundee
1891	Trans.	C. 1905-08	Baly, Edward Charles Cyril, Prof., F.R.S., F.I.C., The University, and 14, Sunnyside, Prince's-park, Liverpool
1914			Bamber, Charles Kelway, The Martyrs, Crawley
1886			Bamber, Henry Kelway George, Ingress House, Greenhithe, Kent
1890	Proc.		Bamber, Montague Kelway, F.I.C., The Laboratory, Hyde-park-corner, Colombo, Ceylon
1916			Bandinel, Thomas James, 104, Trinity-rise, Tulse Hill, S.W.
1914	Trans.		Banerji, Srish Chandra, Agricultural College, Nawabganj, Cawnpore, U.P., India
1910	Proc.		Banerjee, Manindra Nath, Prof., Post Box 431, Calcutta, India
1907			Banks, Arthur John, c/o The Ogilvie Flour Mills Co., Ltd., Montreal, Canada
1911			Barbary, John Ewart Trounce, Vellansaundry, Camborne
1916			Barber, Christopher, 60, Harcourt-road, Sheffield

† Longstaff Medallist, 1912.

Date of Election.			
1904	Trans.	C. 1913-	Barbour, William, M.A. and B.Sc. (St. Andrews), F.I.C., Glenside, Sorbie-road, Saltcoats, BO., Ayrshire
1905			Barbrook, George Henry, c/o Messrs. T. Prentice & Co., Stowmarket, Suffolk
1880			‖Barclay, Arthur Edward, 95, Farringdon-street, E.C.
1903	Trans.		‖Barger, George, M.A. (Cantab.), D.Sc. (Lond.), Malahide, Englefield Green, Surrey
1906			Barker, Arthur Ernest, B.A. and B.Sc. (Lond.), 371, Hagley-road, Edgbaston, Birmingham
1909			Barker, Donald William Elsom, c/o Messrs. E. M. & M. T. Chater, 129, High-street, Watford
1890			‖Barker, Joseph, Rev., M.A. and D.D. (Oxon.), Newton House, Newton, Nottingham
1903	Trans.		Barker, Thomas Vipond, M.A. and B.Sc. (Oxon.), Mineralogical Dept., University Museum, Oxford
1896			Barker, William Henry, B.Sc. (Lond.), Addiscombe, Empress-avenue, Wanstead Park, Essex
1894			Barlet, Stéphane, B. ès Sc. (Gall.), 97, St. Mark's-road, North Kensington, W.
1897			Barlow, Herbert William Leyland, M.A. and M.D. (Oxon.), M.R.C.S. and L.R.C.P. (Lond.), D.P.H., (Cantab.), Holly Bank, Croftsbank-road, Urmston, Manchester
1897	Trans.		Barlow, William, F.R.S., The Red House, Stanmore, Middlesex
1905			Barnes, James Hector, Prof., B.Sc. (Birm.), F.I.C., Government College of Agriculture, Lyallpur, Punjab, India
1875			‖Barnes, Richard Leburn, National Liberal Club, Whitehall, S.W.
1907	Trans.		Barnett, Edward de Barry, B.Sc. (Lond.), A.I.C., 9, Collingham road, South Kensington, S.W.
1912	Trans.		Barnett, Raymond Theodore Fred, B.Sc. (Lond.), A.R.C.S., The Herbert Strutt School, Belper, Derby
1909	Trans.		Baron, Harold, B.Sc. (Vict.), c/o The British Thomson Houston Co., Ltd., 83, Cannon-street, E.C.
1908			Barr, Guy, B.A. (Cantab.), B.Sc. (Lond.), The National Physical Laboratory, Teddington, Middlesex
1888			‖Barraclough, William Herbert, F.I.C., Westholme, Chapeltown, Sheffield
1891			Barratt, John Treeby, 21, Godolphin-road, Helston
1906	Trans.		Barrett, Ernest, B.Sc. (Lond.), 27, Merchiston-road, Catford, S.E.
1901			Barrie, Thomas Stewart, M.B., and Ch.B. (Glas.), 23, Granville-street-west, Charing-cross, Glasgow
1912	Trans.		Barrow, Fred, M.Sc. (Birm.), Ph.D. (Strassburg), Birkbeck College, Breams Buildings, Chancery-lane, E.C.
1905	Trans.		Barrowcliff, Marmaduke, F.I.C., 13, Shirley-road, Nottingham

Date of Election.			
1915			Barry, Thomas Hedley, 9, Napier-avenue, Fulham, S.W.
1912			Barton, Arthur Leslie, 15, Abbotstone-road, Putney Common, S.W.
1872			‖Barton, Robert, Royal Mint, Melbourne, Australia
1908			Barton, Robert, jun., 1431, Ashton Old-road, Higher Openshaw, Manchester
1910			Barwick, Fred Wilkinson, Chamber of Commerce Testing House, Royal Exchange, Manchester
1898			Baskerville, Charles, B.Sc. (Virginia), Ph.D. (N. Carolina), College of the City of New York, New York City, U.S.A.
1864	Trans.	{C. 1870-3, 90-3}	‖Bassett, Henry, F.I.C., 26, Belitha-villas, Barnsbury, N.
1907	Trans.		Bassett, Henry, jun., Prof., D.Sc. (Lond.), Ph.D. (Munich), D. ès Sc. (Nancy), F.I.C., University College, Reading
1911			Bate, Joseph, 59, Southwood-lane, Highgate, N.
1913	Trans.		Bate, Stanley Charles, B.Sc. (Lond.), A.I.C., H.M. Factory, Queen's Ferry, Chester
1891			Bate, William, Upton Villa, Hayle, Cornwall
1913			Bateman, Alan Hamilton, 39, Forest-drive-east, Leytonstone, N.E.
1913	Trans.		Batey, John Percy, M.Sc. Tech. (Manc.), 3, Minorca-road, Weybridge
1896			Bathurst, Charles, M.A. (Oxon.), M.P., Lydney Park, Glos.
1910			Batley, Ward Allen, M.Sc. (Manc.), Northgate, Tickhill, Rotherham
1913			Battye, Horace George, 23, Roman-place, Street-lane, Roundhay, Leeds
1910			Baume, Georges, 14, Avenue du Trocadero, Paris, xv
1914			Baxter, Arthur, B.Sc. (Lond.), Newland Hall, Keresley, Coventry
1914			Baxter, Frederick Stanley, c/o The British Malt Products Co., Lothian House, Market-street, Bermondsey, S.E.
1905			Baxter, John George, Glenarm, Lennox-avenue, Gravesend
1914	Trans.		Baxter, Robert Reginald, B.A. (Oxon.), 18, Wood-street, E.C.
1914			Bayley, Charles Wesley, 63, Caxton-road, Wood Green, N.
1892			Bayliss, Charles, Mino, Hampton-in-Arden, Birmingham
1906			Bayliss, William Heath, Brewery House, Ashwell, Herts.
1874			‖Bayne, James, (unknown)
1879			‖Bayne, William Thirlwall, LL.D. (Cantab.), Brockhill, Broadclyst, Exeter
1891	Trans.		Beadle, Clayton, Oak Bank, Lansdown-road, Sidcup, Kent
1861			‖Beadnell, Charles Edward, Major, R.A., Hafod, Llandinam, Mont.
1903			Beadnell, Charles Marsh, M.R.C.S. (Eng.), L.R.C.P. and L.S.A. (Lond.), Fleet Surgeon, H.M.S. Shannon, Second Cruiser Squadron, c/o G.P.O., London, E.C.

Date of Election.			
1867			Beale, Sir William Phipson, Bart., K.C., M.P., 2, Whitehall-court, S.W.
1903			Beam, William, M.A. and M.D. (Penn.), F.I.C., Chemical Laboratory, Gordon College, Khartoum, Soudan
1899			Bean, Percy, 10, Marsden-street, Manchester
1916	Trans.		Bearder, Ernest Arthur, M.Sc. (Leeds), Mayfield, Wythenshawe-road, Sale, Manchester.
1913			Beath, William, 152, St. George's-road, Hull
1901			Beaven, Edwin Sloper, Eastway, Warminster
1890	Trans.		Beck, Charles Ridgeway, F.I.C., 53, Norroy-road, Putney, S.W.
1874	Trans.		‖Beckett, George Henry, F.I.C., 35, South Beach-road, Ardrossan
1906			Beckett, Richard Henry, Prof., B.Sc. (Lond.), The Victoria College of Science, Nagpur, C.P., India
1901			Bedford, Frederick, B.Sc. (Lond.), Ph.D. (Halle), Dovercourt, Heslington-lane, York
1879	Trans	C. 1895-99 V.-P. 1914-	Bedson, Peter Phillips, Prof., M.A. (Dun.), D.Sc. (Lond. and Dun.), B.Sc. (Vict.), F.I.C., Armstrong College of Science, Newcastle-on-Tyne
1901			Bedwell, John Cardew, B.Sc. (Lond.), c/o Messrs. W. Wesley & Son, 28, Essex-street, Strand, W.C.
1905			Bees, William James, B.Sc. (Lond.), The Red Roofs, Far Headingley, Leeds
1899			Beesley, Frederick Arnold, B.Sc. (Lond.), St. Olave's Grammar School, Tower Bridge, S.E.
1872	Trans.	C. 1907-11 V.-P. 1911-14	‖Beilby, Sir George Thomas, Hon. LL.D. (Glas.), F.R.S., F.I.C., 11, University-gardens, Glasgow
1891			Belbin, Tom St. John, Capt., Nortonthorpe Hall, near Huddersfield
1891			‖Bell, Albert Edward, F.I.C., 151, Camberwell-grove, S.E.
1886	Trans.		Bell, Chichester Alexander, B.A. and M.B. (Dub.), F.I.C., Torbrex, Headington-hill, Oxford
1889			Bell, Edward Wightman, Danum, Spalding
1898			Bell, Hugh Poynter, M.A. (Cantab.), Census and Statistics Office, Ottawa, Canada
1907			Bell, John Forbes, Craigmillar, Edinburgh
1906			Bell, William Edward, c/o Messrs. Tomlinson and Hayward, Manufacturing Chemists, Lincoln
1904	Trans.		Bellars, Albert Ernest, Prof., M.A. (Cantab.), The Government College, Rangoon, Burma
1905			Belton, Francis George, B.A. (Dun.), 342, Belgrave-road, Birmingham
1874			‖Bendix, David, F.I.C., Sutherland Lodge, 371, Romford-road, Forest Gate, E.

Date of Election.			
1902	Proc.		Bengough, Guy Dunstan, M.A. (Cantab.), The University, Liverpool
1902			Benham, Keith Benham, B.Sc. (Lond.), F.I.C., The Universal Grinding Wheel Co., Ltd., Stafford
1881			‖Benjamin, Marcus, A.M. (Lafayette), Ph.B. (Columbia), Ph.D. (Nashville), Sc.D. (Pittsburgh), LL.D. (St. John's Coll., Annapolis), U.S. National Museum, Washington, D.C., U.S.A.
1900	Trans.		Bennett, Alexander Hutcheon, c/o Messrs. G. H. Ogston & Moore, Messina, Sicily
1904			Bennett, Charles Thomas, B.Sc. (Lond.), F.I.C., 16, The Chase, Clapham Common, S.W.
1903			Bennett, Colin Noël, Escot, Penzance, Cornwall
1909	Trans.		Bennett, Hugh Garner, M.Sc. (Leeds), 115, Grove Hill-road, Beverley
1905			Bennett, Joseph, Windsor Printing Co., North Adams, Mass., U.S.A.
1911			Bennison, Ernest Carr, 53, Beaconsfield-road, Cannon-hill, Birmingham
1892	Trans.		‖Bensusan, Arthur John, The Ouro Preto Gold Mines of Brazil, Ltd., Minas de Passagem, Ouro Preto, Brazil
1915			Bentley, John Lloyd, 11, Greenbank-crescent, Darlington
1896	Trans.		Bentley, William Henry, B.Sc. (Vict.), 12, Cromwell-terrace, Irlam, near Manchester
1890			Bentz, Ernest, 30, Manley-road, Manchester
1910			Berens, Herbert Arthur, B.A. (Cantab.), 8, Dawson-place, Pembridge-square, W.
1895	Trans.	C. 1914-	Berkeley, The Rt. Hon. Randal Thomas Mowbray, The Earl of, F.R.S., Foxcombe, Boar's Hill, Oxford
1893			Berridge, Douglas Jesse Penfold, M.A. (Oxon.), The Laboratory, Malvern College, Malvern
1906			‖Berry, Arthur John, M.A. (Cantab.), 14, Regent-street, and Downing College, Cambridge
1882	Trans.		‖Berry, Edward Elhanan, c/o Messrs. Sulman & Picard, 44, London-wall, E.C.; and Vice-Consulate, Bordighera, Italy
1914			Berry, Harry, The Northern College of Pharmacy, Burlington-street, Manchester
1898			Berry, Reginald Arthur, Prof., F.I.C., The West of Scotland Agricultural College, 6, Blythswood-square, Glasgow
1891			Berry, Thomas William, Education Office, Pentre, Rhondda, Glam.
1888	Proc.		Berry, William, 7, Hampton-park, Redland, Bristol
1909	Trans.		Best, Stanley Robert, M.Sc. (Manc.), Woodlands, 41, Egerton-road, Chorlton-cum-Hardy, Manchester
1906			Bethea, Oscar Walter, Prof., M.D. (Miss. and Tulane), Ph.G. (Atlanta), 1735, Corrollton-avenue, New Orleans, La., U.S.A.

Date of Election.			
1910			Bethwaite, John, Ashgrove, Workington
1883	Trans.	{C. 1898-1900, 1913-15.}	‖Bevan, Edward John, F.I.C., 3, New-court, Carey-street, W.C.
1886			Bevan, John Williams, F.I.C., c/o Morriston Spelter Works, Morriston, Glam.
1903			Beveridge, Wilfred William Ogilvy, Lieut.-Col., R.A.M.C., D.S.O., M.B. (Edin.), D.P.H. (Cantab.), Head Quarters, I.G.C., France
1912			Bews, Charles James Vinall, B.Sc. (Lond.), A.R.C.S., 45, Northfield-road, King's Norton, Birmingham
1897			Bhaduri, Jyoti Bhushan, M.A. (Calcutta), Presidency College, Calcutta, India
1903			Bhaduri, Kula Bhushan, Prof., M.A. (Calcutta), Canning College, Lucknow, India
1916			Bhathena, Nowrosji Maneckji, Livingston Hall, Columbia University, New York City, U.S.A.
1903			Bibby, Robert Gordon, B.A. (Oxon.), 5, Half Moon-street, W.
1865			‖Bickerdike, William Edward, F.I.C., Bryers Croft, Wilpshire, Blackburn
1908			Bickerstaffe, Robert, Wynstay, St. Anne's-road, Blackpool
1901			‖Bickford, Harding, 46, Currie-street, Adelaide, South Australia
1914			Bicknell, Arthur, B.Sc. (Manc.), Balliol College, Oxford
1875			Biggart, John William, F.I.C., Chemical Laboratory, 29, Cathcart-street, Greenock
1913			Biggart, William Love, Rossarden, Kilmacolm, Renfrewshire
1881			‖Bingley, John, Northampton
1900			Binks, Frederick Nisbet, 5, East-avenue, Benton, Newcastle-on-Tyne
1908			Birch, William Colet, B.A. (Cantab.), F.I.C., The Chemical Laboratory, P.O. Box 141, Nairobi, British East Africa
1894			Bird, William Rowland, Chem. Lab., G.W.R. Works, Swindon
1912			Birks, Cyril Douglas, Cobnar-gardens, Woodseats, Sheffield
1906			Birt, Roderick Harold Capper, Rev., B.A. (Oxon.), St. Peter's College, Radley, Abingdon
1914			Bishop, Robert Odell, Axham House, Rye
1913	Trans.		Bissett, Crellyn Colgrave, B.A. (Cantab.), B.Sc. (Lond. and Sheffield), B.Met. (Sheffield), Pinehurst Grange, Farnborough, Hants.
1904			Black, John Wyclif, 62, Falcon-avenue, Edinburgh
1909			Blackburn, Albert Riley, B.Sc. (Lond.), A.R.C.S., The Grammar School, Staveley, Chesterfield
1913			Blackburn, George Frederick William, c/o Mrs. Caske, 27, Cartvale-road, Langside, Glasgow

Date of Election.		
1911		Blackburn, Joseph Mayson, 22, Hodford-road, Golders Green, N.W.
1911		Blackhurst, Arthur Owen, N.D.A., Square-lane, Latham, Ormskirk
1899	Trans.	Blackman, Walter Lionel, Mostyn, Stanthorpe-road, Streatham, S.W.
1903		Blackshaw, George Neville, B.Sc. (Wales), Analytical Laboratory, Dept. of Agriculture, Salisbury, Rhodesia, S. Africa
1912	Proc.	Blackstock, Gibbs, M.A. (Toronto), 53, Bloxcidge-street, Langley, Birmingham
1914		‖Blair, Ethelbert William, B.Sc. (Lond.), 70, Fountayne-road, Stoke Newington, N.
1902		Blair, Herbert, 134, Ashley-road, West Harton, South Shields
1901		Blake, George Stanford, 25, Curwen-street, Workington
1890	Trans.	Blake, Robert Frederick, F.I.C., County Analyst's Laboratory, Scottish Provident-buildings, Belfast
1890		Blake, William Henry, 12, Lombard-street, Newcastle-on-Tyne
1875		‖Blanshard, Charles Thomas, M.A. (Oxon.), School House, Keswick
1906		Blatchley, Charles Frederick Polwhele, B.A. (Oxon.), Littlebere, Cheam, Sutton
1913		Blaxter, Augustus Pearce Llewellyn, B.A. (Cantab.), Chidham, Potters Bar, Middlesex
1892		Bleckly, Arthur Sanderson, Marldon, Thelwall, Warrington
1902		Blenkinsop, Richard, c/o Messrs. May & Baker, Ltd., Garden Wharf, Church-road, Battersea, S.W.
1909		Bletcher, Henry Ernest John, Prof., College of Pharmacy, Winnipeg, Manitoba, Canada
1916	Trans.	Bleuler, Hanns, Ph.D. (Berne), 161, Hyde Park-road, Leeds
1903		Bliss, Henry James Wheeler, M.A. (Oxon.), 50, City-road, E.C.
1899		Blofeld, Stuart, Rev., B.A. and B.Sc. (Lond.), Saltley Training College, Birmingham
1896		‖Blood, Maurice, M.A. (Oxon.), 51, Winchester-avenue, Kilburn, N.W.
1891		Bloomer, Frederick John, F.I.C., Penpont, Clydach, Glamorgan
1890	Trans.	Blount, Bertram, F.I.C., 76 and 78, York-street, Westminster, S.W.
1888		Bloxam, Arthur George, F.I.C., Room 105, 29, Southampton-buildings, Chancery-lane, W.C.
1903		Bluman, Nicholas John, 14, Alba-gardens, Golders Green, N.W.
1887		Blundstone, Edwin Richardson, B.A. (Cantab.), 79, York-street, Westminster, S.W.
1865	Trans.	Blunt, Thomas Porter, M.A. (Oxon.), F.I.C., Tower-place, Shrewsbury
1896		Blyde, Joseph Edwin Alger, East Cliffe, East Bank-road, Sheffield
1875	Trans.	Blyth, Alexander Wynter, M.R.C.S. (Eng.), L.S.A. (Lond.), F.I.C., 5, Woodchurch-road, Hampstead, N.W.

Date of Election.			
1892			Blyth, Meredith Wynter, B.A. (Cantab.), B.Sc. (Lond.), F.I.C., Lacton House, Tanbersley, near Barnsley
1908	Trans.		Blyther, Donald Francis, B.Sc. (Lond.), A.R.C.S., 7, Airthrie-road, Goodmayes, Ilford
1875			‖Boake, Arthur, Chemical Works, Stratford, E.; and High-standing, Loughton, Essex
1902			Boardman, Ernest, B.Sc. (Vict.), 3, Glade-street, Bolton
1898			Bogert, Marston Taylor, Prof., B.A. and Ph.B. (Columbia), Hon. LL.D. (Clark), Columbia University, New York City, U.S.A.
1906			Bogue, Thomas Going Stoney, 5, Kenilworth-square, Dublin
1869	Trans.		‖Bolas, Thomas, F.I.C., 60, Grove-park-terrace, Chiswick, W.
1901			Bolton, Edward Richards, F.I.C., 46, Stamford Brook-road, Hammersmith, W.
1899			‖Bond, Alfred Ernest, 13, Hermitage-road, Edgbaston, Birmingham
1915			Bone, Samuel Culloch, 30, Long-lane, Garston, Liverpool
1893	Trans.	C. 1909-13	‖Bone, William Arthur, Prof., D.Sc. (Vict.), Ph.D. (Heidelberg), F.R.S., The Imperial College of Science and Technology, S. Kensington, S.W.; and Montrose, Harpenden-road, St. Albans
1912			Bones, Arthur Anderson, P.O. Box 1323, Market-buildings, Pretoria, Transvaal, S. Africa
1914	Trans.		Boon, Alfred Archibald, D.Sc. (Edin.), F.I.C., 87, Warrender-park-road, Edinburgh
1893			Boone, William Thomas, B.A. and B.Sc. (Lond.), 6, Sydenham-villas, Cheltenham
1884			Borland, William Dalrymple, F.I.C., Beacon Lodge, Green Street Green, Dartford, Kent
1881			‖Borns, Henry, Ph.D. (Greifswald), 5, Sutton Court-road, Chiswick, W.
1895			‖Borradaile, Lancelot Alexander, M.A. (Cantab.), Selwyn College, Cambridge
1914			Bose, Adhor Krishna, 90, Musjeed Baree-street, Calcutta, India
1894	Proc.		Bose, Chuni Lal, Prof., 25, Mohendra Bose's-lane, Calcutta, India
1881			Bostock, George Henry, 441, Wellesley-street, Toronto, Canada
1910			Bosworth, Stewart McGregor, B.Sc. (Lond.), 55, Abingdon-road, Kensington, W.
1881	Trans.		Bothamley, Charles Herbert, M.Sc. (Leeds), F.I.C., Weston-super-Mare
1887	Trans.		Bott, William Norman, Ph.D. (Heidelberg), c/o Messrs. Brotherton & Co., Ltd., Litherland, Liverpool
1909			Bottomley, Hubert Frederick, c/o Messrs. Sanitas Co., Ltd., Limehouse, E.
1869			‖Bottomley, James Thomson, B.A. (Dub.), M.A. and D.Sc. (R.U.I.), Hon. LL.D. (Glas.), F.R.S., 13, University-gardens, Glasgow

Date of Election.			
1886			Bottomley, William Beecroft, Prof., M.A. (Cantab.), Ph.D., 35, Downside-crescent, Hampstead, N.W.
1910	Trans.		Bourdillon, Robert Benedict, B.A. (Oxon), University College, Oxford
1905	Trans.	C. 1911-14	Bousfield, William Robert, M.A. (Cantab.), K.C., F.R.S., St. Swithin's, Hendon
1891			Bovell, John Redman, I.S.O., Department of Agriculture, Barbados, West Indies
1912	Trans.		Bowack, Douglas Anderson, 15, Belsize-square, Hampstead, N.W.
1912			Bowater, William Henry, School of Mines, Charters Towers, Queensland
1911	Trans.		Bowden, Richard Charles, M.Sc. (Bristol), Royal Gunpowder Factory, Waltham Abbey, Essex
1865			‖Bowdler, Arthur Clegg, F.I.C., 20, Bank-terrace, Wellington-street, Blackburn
1914			Bowell, Arthur Henry, University College, Auckland, New Zealand
1888			Bower, Frank, c/o Messrs. Truman, Hanbury and Buxton, Spital-fields, E.
1894			Bowes, Harry, F.I.C., Messrs. Bowes and Sims, 40, Radford-street, Blackley, Manchester
1906			Bowis, William John, Ph.D. (Zürich), 9, Rectory-road, West Bridgford, Nottingham
1899			Bowles, Bertram Hennessey, Overdale, Eastwood-road, South Woodford, N.E.
1896			Bowley, Joseph John, Wellington Works, Battersea Bridge, S.W.
1896			‖Bowman, Herbert Lister, Prof., M.A. and D.Sc. (Oxon.), Magdalen College, Oxford
1911			Bowyer, Arthur Stewart, M.Sc. (Manc.), The Woodlands, Chelford, Cheshire
1914			Boyd, Alexander John, A.I.C., c/o Miss Anson, 28, Colbourne-road, Hove, BO., Brighton
1894	Trans.		Boyd, David Runciman, Prof., D.Sc. (Glas.), Ph.D. (Heidelberg), F.I.C., University College, Southampton
1910			Bracewell, Geoffrey Alfred, A.I.C., 17, Farcliffe-terrace, Bradford
1910			Bracher, André, 7, Cambridge-mansions, Battersea Park, S.W.
1903			Bradbury, Samuel, Ferncliff, Milton-grove, Glebelands-road, Ashton-on-Mersey, Cheshire
1895			Bradford, Henry, Strettington, Chichester
1888			Bradshaw, Charles, 17, Crimicar-lane, Fulwood, Sheffield
1914	Trans.		Bradshaw, John, M.Sc. (Manc.), Vernon House, Monument-park, Wigan

Date of Election.		
1910	Trans.	Brady, Oscar Lisle, D.Sc. (Lond.), B.A. (Cape of Good Hope), A.I.C., D.I.C., Research Dept., Royal Arsenal, Woolwich, S.E.
1908		Brakes, William Sudderick, 119, Steade-road, Sheffield
1894	Trans.	Brame, John Samuel Strafford, Prof., Royal Naval College, Greenwich, S.E.
1913	Trans.	Bramley, Arthur, D.Sc. (Lond.), A.R.C.S., A.I.C., 87, Elizabeth-street, Elland, Yorks.
1903		Branch, George Thomas, P.O. Box 112, Salisbury, Rhodesia, S. Africa
1916		Branson, Frederick Hartridge, Myrtle Cottage, Talbot-road, Roundhay, Leeds
1882		Branson, Frederick Woodward, F.I.C., 14, Commercial-street, Leeds; and Wynneholme, Far Headingley, Leeds
1896		Bray, Daniel, 5, Weirwood-park, Bailleston, Glasgow
1915	Trans.	Brazier, Sidney Albert, M.Sc. (Birm.), 2, Mansfield-villas, Yardley Wood-road, Moseley, Birmingham
1909		Breakspear, Henry Shaw, B.A. (Oxon.), The Grammar School, Ludlow
1913		Brearley, Arthur Joseph, B.A. (Cantab.), 13, Victoria-terrace, Exeter
1905		‖Brettell-Vaughan, Edward Shipley Hewitt Edwards, 160, Plashet-grove, East Ham, E.
1883		Briant, Lawrence, 24, Holborn-viaduct, E.C.
1901		Bridges, Joseph Samuel, B.Sc. (Lond.), M.A. and LL.D. (Cantab.), Barrister-at-Law, 23, Anson-road, Cricklewood, N.W.
1913		Brier, Albert, M.Sc. (Leeds), B.Sc. (Manc.), 19, Alexander-road, Ulverston
1897		Brierley, James, 33 and 35, French-street, Southampton
1890	Trans.	Brierley, John Thomas, Highfield, Golden Hill, Leyland, Preston
1898		Brierley, Joseph, B.Sc. (Vict.), 13, Kershaw-street, Failsworth, Manchester
1910		Briggs, John Cockbain, Lieut., Commd. Coalville Detachment, 3/5 Battn. Leicestershire Regiment, Labour Exchange, Coalville, Leicester
1893	Trans.	Briggs, John Frederick, Auchmuty Paper Mills, Markinch, Fife
1906		Briggs, Richard Victor, P.O. Box 279, 8, Lall Bazar-street, Calcutta, India
1905	Trans.	Briggs, Samuel Henry Clifford, D.Sc. (Vict.), Croft Villa, Gomersal, Leeds
1883		‖Briggs, Thomas Lynton, F.I.C., 188, Central-avenue, Flushing, L.I., U.S.A.

Date of Election.			
1884			‖Briggs, William, LL.D., D.C.L., M.A., B.Sc., Burlington House, Cambridge
1912			Brindle, Harry, Manchester College of Pharmacy, 225A, Oxford-road, Manchester
1914	Trans.		Brinsley, Frank, M.Sc. Tech. (Manc.), Huguenot College, Wellington, Cape Province, S. Africa
1910	Trans.		Briscoe, Henry Vincent Aird, D.Sc. (Lond.), A.R.C.S., 40, Cyril Mansions, Prince of Wales-road, Battersea Park, S.W.
1889			Broadbent, Harry, F.I.C., 9, Bainbridge-road, Leeds
1879			‖Broadbent, John James, F.I.C., Waikino, Ohinemari, Auckland, New Zealand
1893			‖Brockbank, John Edwin, The Croft, Kirksanton, viâ Carnforth
1915			Brodie, Neal, B.Sc. (Dun.). Government Test House, 30, Judges' Court-road, Alipore, Calcutta, India
1915			Bromwich, William Alfred, 4, Lambeth Palace-road, S.E.
1900			Brooke, Charles Berjen, Colne House, Brantham, Manningtree, Essex
1900			Brooke, John Richard, J.P., F.I.C., Government Opium Factory, Singapore, Straits Settlements
1913			Brooks, Archibald Joseph, Melrose, St. Lucia, British West Indies
1906			Broome, James Spears, M.Sc. (Manc.), Penshurst, Hill Cliffe, Warrington
1886	Trans.		‖Brothers, Horace Edward, B.Sc. (Lond.), F.I.C., Clooney, Higher Knutsford-road, Latchford, Warrington
1876	Trans.	C. 1910-13	Brown, Adrian John, Prof., M.Sc. (Birm.), F.R.S., F.I.C., West Heath House, Northfield, Birmingham
1867	Trans.	C. 1872-4, V. P. 81-4, 90-1, P. 91-3	Brown, Alexander Crum, Prof., M.A., M.D., and F.R.C.P. (Edin.), D.Sc. (Lond.), LL.D. (Aberd. and Glas.), Hon. LL.D. (St. Andrews), F.R.S., F.I.C., 8, Belgrave-crescent, Edinburgh
1870			Brown, David, F.I.C., 93, Abbey-hill, Edinburgh
1873	Trans.	C. 1881-3	‖Brown, Frederic Douglas, Prof., B.Sc. (Lond.), 3, Norton-road, Hove, BO., Brighton
1884			Brown, Frederic William, Ingleside, 39, Loveday-road, West Ealing, W.
1892			Brown, George Fitz-, A.R.S.M., F.I.C., The Broughton Copper Co., Ditton Copper Works, Widnes
1897			Brown, Gerald Noël, Bonnington, near Nelson, British Columbia
1880		C. 1883-7, V. P. 1894-7, 1904-7, 1913-16 T. 1903-04 F.S. 1907-13	Brown, Henry, F.I.C., Benskin's Brewery, Watford, Herts.
1871	Trans.		†Brown, Horace Tabberer, LL.D. (Edin.), F.R.S., F.I.C., 52, Nevern-square, Kensington, S.W.

† Longstaff Medallist, 1894.

Date of Election.		
1908		Brown, James, 20, Tower-road, Dartford, Kent
1914		Brown, James Meikle, B.Sc. (Lond. and Sheffield), 176, Carter Knowle-road, Sheffield
1882		Brown, Reginald Busby, 45, Finsbury-square, E.C.
1908		Brown, Walter, jun., County Offices, Hamilton
1884		Brown, William George, Prof., Ph.D. (N. Carolina), B.S. (Virginia), University of Missouri, Columbia, Missouri, U.S.A.
1893		Browne, Frank, F.I.C., 60, Fornham-road, Bury St. Edmund's
1873		Brownen, George, Grove-road-east, Avon-park, Christchurch
1899	Trans.	Browning, Kendall Colin, Prof., M.A. (Cantab.), Medical College, Colombo, Ceylon
1912		Brownlie, David, B.Sc. (Lond.), 41, Corporation-street, Manchester
1890		Brownsword, Frank, M.Sc. (Vict.), F.I.C., Bryn Derwen, Old Colwyn, N. Wales
1902		Bruce, Alexander, B.Sc. (Edin.), The Laboratory, Hyde-park-corner, Colombo, Ceylon
1894	Trans.	‖Bruce, James, B.Sc. (Lond.), Ph.D. (Munich), A.R.C.S., F.I.C., The Technical College, Huddersfield
1901		‖Bruce-Kingsmill, Julian, Major, R.A., M.A. and B.Sc. (Glas.), 7, The Barons, East Twickenham
1903		Brühl, Paul, Senate House, College-square, Calcutta, India
1898	Trans.	‖Brünnich, Johannes Christian, F.I.C., Department of Agriculture, Brisbane, Queensland
1912		Brunjes, Thomas Alfred, 94, Waller-road, New Cross, S.E.
1893	Trans.	‖Brunton, John Dixon, c/o Prof. O. W. Richardson, F.R.S., 4, Cannon-place, Hampstead, N.W.
1914		Bryant, Edward Godfrey, B.A. and B.Sc. (Lond.), Grey Institute, Port Elizabeth, S. Africa
1912		Bryant, Ernest Gower, 100, Burlington-street, Manchester
1902		Bryant, Vernon Seymour, M.A. (Cantab.), Trelawne, Crowthorne, Berks.
1877	Trans.	Buchanan, John Young, M.A. (Cantab.), F.R.S., F.I.C., 26, Norfolk-street, Park-lane, W.
1912		‖Buckle, Edmund Arthur, 8, Waterloo-place, S.W.
1876		‖Buckmaster, Charles Alexander, M.A. (Oxon.), 16, Heathfield-road, Mill Hill Park, Acton, W.
1902		Bucknell, Edwin Thomas Holman, Kingsholme School, Weston-super-Mare
1907	Trans.	Buckney, Frank, B.A. (Cantab.), Custom House, Calcutta, India
1903		Buggé, Erasmus Robert, Instow, Mycenae-road, Westcombe Park, S.E.

Date of Election.		
1911		Bull, Bertram Alfred, 14, North-road, West Bridgford, Nottingham
1911		Bull, Joseph Beauchamp, Box 445, Bulawayo, S. Africa
1901		Bult, Herbert John, 63, Addiscombe-road, Croydon
1912		Bunker, Sidney Waterfield, B.Sc. (Lond.), A.I.C., Department of Agriculture, Kuala Lumpur, Federated Malay States
1890		‖Bunting, Henry Herbert, Oficina de Ensayes F. C. C. del Peru, Callao, Peru
1896		Burbridge, James Kerry, F.I.C., The Orchard, Philip-lane, Tottenham, N.
1911		Burbridge, Walter Norman, 14, Granville-road, Watford
1891		Burford, Samuel Francis, The Ridgeway, Rothley, Leicester
1894	Trans.	Burgess, Herbert Edward, Holly House, Graham-road, N.E.
1901		Burgess, Percival James, M.A. (Cantab.), 62, Norfolk-road, Littlehampton
1884		Burgess, William Thomas, F.I.C., 20, Priory-road, Bedford Park, W.
1903		Burghard, William Godsell, 43, New Oxford-street, W.C.
1897		Burland, Richard Oxley, J.P., Poolstock House, Wigan
1901		‖Burnett, Theodore Ridley, B.Sc. (Vict.), Ph.D. (Bâle), The George Green's School, East India Dock-road, Poplar, E.
1893		Burnham, John Charles, C.S.I., B.Sc. (Vict.), F.I.C., Cordite Factory, Aruvankadu, Nilgiri Hills, India
1882	Trans.	Burrell, Benjamin Arthur, F.I.C., 8, Springfield Mount, Leeds
1901	Trans.	Burrows, Merrick William, M.Sc. (Vict.), Dunkirk, Devizes
1905	Trans.	Burt, Bryce Chudleigh, B.Sc. (Lond.), Department of Agriculture, Cawnpore, India
1909	Trans.	Burt, Frank Playfair, D.Sc. (Bristol), B.Sc. (Lond.), 15, Oak-road, Withington, Manchester
1891		Burton, William, Clifton Junction, near Manchester
1916		Burton, William Arthur Graham, Claymer, Bushey Wood, Totley Rise, Sheffield
1912		Bury, Charles Rugeley, B.A. (Oxon.), Chemical Laboratories, University College of Wales, Aberystwyth
1903		Bury, Ernest, M.Sc. (Vict.), Queensmede, Saltburn-by-the-Sea
1884		‖Bush, Richard Arthur, Holt, Morden, Mitcham
1894		Bush, William, School of Science and Art, Free Library, Newport, Mon.
1915		Bush, William Arthur, Holt, Morden, Mitcham
1895		Butler, David Butler, 6, Earl-street, Westminster, S.W.
1913		Butler, George Bernard, Adelaide Villa, Belle Vue-grove, Grove Hill, Middlesbrough
1916		Butler, Raymond Renard, 27, Castle Bar-road, Ealing, W.

Date of Election.		
1890		Butler, William Waters, Southfield, Norfolk-road, Edgbaston, Birmingham
1894		Buttemer, Robert William, St. Mary's, Godalming, Surrey
1875		Butterfield, John Cope, F.I.C., 79, Endlesham-road, Balham, S.W.
1892		Butterfield, William John Atkinson, M.A. (Oxon.), F.I.C., 66, Victoria-street, S.W.
1910	Trans.	Buttle, Bertram Haward, 63, Claremont-road, Forest Gate, E.
1902		Buxy, Tarit Kanti, Prof., Govt. College, Jubbulpore, C.P., India
1888		Byrn, George Alexander, F.I.C., Reiby Chambers, Reiby-lane, Circular Quay, Sydney, N.S.W.
1906		Byrom, Thomas Henry, F.I.C., The Virol Research Laboratories, 10, Bedford-square, W.C.
1903		Bywaters, Hubert William, D.Sc. (Lond. and Bristol), Ph.D. (Würzburg), A.R.C.S., F.I.C., 9, Henleaze-avenue, Bristol
1913	Trans.	‖Cahen, Edward, A.R.C.S., F.I.C., Chemical Dept., St. Bartholomew's Hospital, E.C.
1893		‖Cahill, Robert Saunderson, Sunnyside, Heckmondwike
1894	Trans.	‖Cain, John Cannell, D.Sc. (Vict. and Tübingen), 24, Aylestone-avenue, Brondesbury Park, N.W.
1906		Calam, Harold, M.Sc. (Leeds), B.Sc. (Manc.), F.I.C., 18, Melton-road, West Bridgford, Nottingham
1891		‖Calder, William Alexander Skeen, 449, Hagley-road, Birmingham
1907	Trans.	Caldwell, Kenneth Somerville, Prof., B.Sc. (Wales), Ph.D. (Leipzig), F.I.C., Patna College, Bankipore, India
1906	Trans.	Caldwell, William, Prof., M.A. (R.U.I.), M.A., Sc.D. (Dub.), F.I.C., Royal College of Surgeons in Ireland, St. Stephen's Green, Dublin
1884		Caley, Edward James, Chapel Field Works, Norwich
1907	Trans.	Callan, Thomas, M.Sc. (Manc.), Ph.D. (Heidelberg), 26, Perrymead, Prestwich, Manchester
1909		Callister, William Edward, B.Sc. (Manc.), 2, Victoria-avenue, Onchan, Douglas, Isle of Man
1914		Calvert, Albert Frederick, Royston, Eton-avenue, N.W.
1903	Trans.	Calvert, Harry Thornton, Ph.D. (Leipzig), M.Sc. (Leeds), B.Sc. (Vict.), F.I.C., c/o The Ministry of Munitions, Dept. of Explosives Supplies, Storey's Gate, Westminster, S.W.
1907	Trans.	Cameron, Alexander Thomas, M.A. and B.Sc. (Edin.), Lieut. R.A.M.C. Mess, Grosvenor-road, S.W.
1910		Camp, Frank Anthony, c/o Deccan Sugar and Abkari Co., Ltd., Samalkot, Godavari Dist., India
1912		Campbell, Alfred Varlow, A.C.G.I., The Croft, St. James'-road, Harpenden, Herts.

Date of Election.		
1892		Campbell, Andrew, 1, Park-road, Beckenham
1912	Trans.	Campbell, Arthur Fred, M.Sc. (Manc.), 9, Fort-road, Sedgley Park, Manchester
1913	Trans.	Campbell, Bertram, B.Sc. (Lond.), A.I.C., D.I.C., The Chemical Laboratories, Royal Aircraft Factory, South Farnborough, Farnborough, Hants.
1913	Trans.	Campbell, Norman Phillips, B.A. (Oxon.), A.I.C., St. Margarets, Burgess Hill, Sussex
1903		Campbell, Thomas, c/o Messrs. Campbell, Garrick & Co., 13, Hewer-street, Notting Hill, W.
1898		Campion, Alfred, Prof., F.I.C., The Royal Technical College, Glasgow
1896		Candy, Hugh Charles Herbert, B.A. and B.Sc. (Lond.), F.I.C., The College, London Hospital, E.
1915		Canning, Joseph Herbert, Crindau Gasworks, Newport, Mon.
1893		Cannon, Matthew James, 16 and 17, Devonshire-square, Bishopsgate-street, E.C.
1910		Canton, Howard, Brockenhurst, Finchley-road, Golder's Green, N.W.
1910		Cardoso, Ettore, D. ès Sc. (Grenoble), Istituto Chimico Farmaceutico, Regia Universita, San Marcellino, Naples, Italy
1888		Carey, Alfred Edward, M.Inst.C.E., 36, Victoria-street, S.W.
1892	Trans.	Carey, Arthur, B.Sc. (Vict.), 1, Grassendale-road, Grassendale, Liverpool
1906		Carmichael, John, Government Laboratory, Clement's Inn-passage, Strand, W.C.
1911		Carmichael, John Fisher, B.Sc. (Vict.), Tower Building, Liverpool
1902		Carmichael, Thomas Burnell, 64A, South-road, Waterloo, Liverpool
1889		Carmody, Patrick, Prof., F.I.C., Department of Agriculture, Port of Spain, Trinidad
1916		Carpenter, Charles William, M.Sc. Tech. (Manc.), 7, Unity-road, Stowmarket
1899	Trans.	‖Carpenter, Henry Cort Harold, Prof., M.A. (Oxon.), Ph.D. (Leipzig), 30, Murray-road, Wimbledon Common, S.W.
1906		Carpenter, Percy Henry, F.I.C., Tocklai Experimental Station, Cinnamara, P.O., Assam, India
1899		Carpmael, Wilfred, 24, Southampton-buildings, Chancery-lane, W.C.
1895	Trans.	‖Carr, Francis Howard, F.I.C., Westhorpe, Ruddington, Nottingham
1887		Carrington, George Carrington, Missenden Abbey, Great Missenden, Bucks.
1902		Carrodus, Fred, Glen Cairn, The Ridgway, Wimbledon, S.W.

Date of Election.			
1893			Carswell, Thomas Retson, 1, Mardy Villas, West-street, Leigh on-Sea, Essex
1913			Carter, Frederick George, Amritsar Distillery, Amritsar, Punjab, India
1867			‖Carulla, Facundo Joaquin Ramon, Argyll-terrace, 84, Rose-hill street, Derby
1913			Caruth, Alexander, A.R.C.S., 101, Singleton-avenue, Prenton, Birkenhead
1895			Case, Thomas Bennett, B.A. (Oxon.), Brewers' Laboratory, Messrs. Guinness, Son & Co., Dublin
1879			‖Cassal, Charles Edward, Col. V.D., F.I.C., Town Hall, Kensington, W.
1903			‖Caudwell, Ben, B.A. (Lond.), 29, Sale-hill, Sheffield
1909			Caulkin, Howard Alfred, B.Sc. (Lond.), F.I.C., The Glen, Cumberhill-road, Duffield, Derby
1898	Trans.		Caven, Robert Martin, D.Sc. (Lond.), F.I.C., University College, Nottingham
1912			Chakraborty, Jatindranath, B.A. (Calcutta), 57, Talpukar-road, Beleghata P.O., Calcutta, India
1902			Challen, Matthew Bradbury, Daylesford Technical School, Daylesford, Victoria, Australia
1910	Trans.		Challenger, Frederick, B.Sc. (Lond.), Ph.D. (Göttingen), F.I.C., The University, Edmund-street, Birmingham
1912			Challinor, Richard Westman, F.I.C., Quidington, Emmerick-street, Leichhardt, Sydney, N.S.W.
1874			Chaloner, George, South-street, Colyton, Devon
1906			Chamberlain, Percy Garratt, M.A. (Cantab.), 3, Market-place, Rugby
1909			Chambliss, Hardee, Prof., M.S. (Vanderbilt), Ph.D. (Johns Hopkins), Department of Chemistry, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma, U.S.A.
1883			‖Chambres, Gordon Crewe, Rev., M.A. (Oxon.), 31, Upper Diconson-street, Wigan
1883			‖Chance, Alexander Macomb, J.P., Messrs. Chance and Hunt, Ltd., Chemical and Cement Works, Oldbury, Birmingham
1902			‖Chance, Kenneth Macomb, M.A. (Cantab.), c/o The British Cyanides Co., Ltd., Oldbury, Birmingham
1872			‖Chandler, Charles Frederick, Prof., Ph.D. (Göttingen), Columbia University, West 116th-street, New York City, U.S.A.
1889			‖Chaplin, Edward Mitchell, Ph.D. (Würzburg), F.I.C., Public Analyst's Office, Wakefield
1886	Trans.	C. 1908-10, 1916–	Chapman, Alfred Chaston, F.I.C., 8, Duke-street, Aldgate, E.C.
1895			Chapman, Arthur Jenner, F.I.C., c/o Messrs. F. Claudet, Ltd., 6 and 7, Coleman-street, E.C.

Date of Election.			
1898	Trans.	C. 1915–	‖Chapman, David Leonard, M.A. (Oxon.), F.R.S., Jesus College, Oxford
1899	Trans.		Chapman, Edgar Marsh, F.I.C., 65, Scalby-road, Scarborough
1891			Charles, Rhys Pendrill, F.I.C., Bacteriological Laboratory, King's College, Strand, W.C.
1911			Charlton, Edwin Johnson, M.Sc. (Manc.), Belmont, Beaumaris, Anglesey
1900			Chater, Arthur Brand, 65, Queen-street, Brisbane, Queensland
1894	Trans.	C. 1900-03	‖Chattaway, Frederick Daniel, M.A. (Oxon.), D.Sc. (Lond.), Ph.D. (Munich), B.Sc. (Birm.), F.R.S., F.I.C., 151, Woodstock-road, Oxford
1915			Chatterji, Manmatha Nath, L. H. Sugar Factory, Pilibhit, U.P., India.
1914			Chattopadhyay, Proboda Chundra, M.A. (Calcutta), 90, Maniktala Main-road, Harrison-road P.O., Calcutta, India
1895			Cheadle, Walter William, M.A. (Oxon.), Woodlands, Bridge-road, Grays
1899			Cheater, Thomas John, B.Sc. (Lond.), 18, Queen Anne's-grove, Bedford Park, W.
1900			Cheeseright, John Henry, B.Sc. (Lond.), Secondary School, Gateshead-on-Tyne
1915			Cheng, Pinzen, B.Sc (Birm.), A.I.C., Kia-ting-hsien, near Shanghai, China
1912			Cheshire, Frank Lothian, Mines Dept., Brisbane, Queensland, Australia
1908			Chew, John Henry, 266, Lytham-road, Blackpool
1897	Trans.		Chikashigé, Masumi, D.Sc. (Kyoto), College of Science and Engineering, Imperial University, Kyoto, Japan
1897			Cholerton, Alfred Foster, c/o Messrs. A. de St. Dalmas & Co., 40½, Belgrave-gate, Leicester
1891	Trans.		‖Chorley, John Christmas, Bewsey, Oxford-road, Birkdale, Lancs.
1913			Chowdry, Santi Pada, 5/2, Mohes Chandra Chowdry Lane, Bhowanipur, Calcutta, India
1907			‖Christie, John, B.A. (Cantab.), Eton College, Windsor
1913			Christie, John Hugh, B.Sc. (Lond.), A.I.C., c/o Dr. Bean, Cross Gates, Leeds
1874			Christopher, George, Walkden Works, Verney-road, Bermondsey, S.E.
1911	Trans.		Christopher, Harold, B.Sc. (Lond.), c/o Messrs. Joseph Crosfield & Sons, Ltd., Warrington
1882			Chrystal, William James, F.I.C., 7, West George-street, Glasgow; and Shawfield Works, Rutherglen, near Glasgow

Date of Election.		
1906	Trans.	Chrystall, Edwin Rodney, B.Sc. (Lond.), F.I.C., c/o Messrs. Curtis's and Harvey, Explosives Works, Cliffe-at-Hoo, Kent
1901	Trans.	Clark, Ernest, B.Sc. (Lond.), Royal Technical Institute, Salford
1892		Clark, Ernest Victor, 2, St. Anne's-villas, Lewes
1913		Clark, Francis William, 35, Wilmington-square, W.C.
1905		Clark, Friend Ebenezer, Prof., B.Sc. (West Virg.), Ph.D. (Johns Hopkins), Dept. of Chemistry, West Virginia University, Morgantown, W. Virginia, U.S.A.
1916		Clark, John Archibald, 11, Walmer-terrace, Ibrox, Glasgow
1916		Clark, Joseph George, 64, Hewitt-road, Harringay, N.
1912		‖Clark, Leslie Melville, 3, Harley-road, Hampstead, N.W.
1905		Clark, Thomas Walter Firth, Tilehurst, Pollard-road, Mitcham
1911		Clarke, Arthur Frederick, 218, Nelson-road, Gillingham, Kent
1909	Trans.	Clarke, George, F.I.C., Department of Agriculture, Cawnpore, U.P., India
1908	Trans.	‖Clarke, Hans Thacher, D.Sc. (Lond.), F.I.C., c/o The Eastman Kodak Co., Kodak Park, Rochester, N.Y., U.S.A.
1910	Trans.	Clarke, Herbert Edmund, M.A. and B.Sc. (Oxon.), 20, Grosvenor-road, Jesmond, Newcastle-on-Tyne
1906	Trans.	Clarke, Reginald William Lane, B.Sc. (Lond.), F.I.C., 15, Torridon-road, Catford, S.E.
1912		Clarke, William Thomas, B.Sc. (Lond.), Ormonde House, Cross-hill, Codnor, Derby
1905		Clarkson, George Douglas, Hollindon, St. Paul's-road, Mirfield, Yorks.
1909	Trans.	Clayton, Arthur, D.Sc. (Lond.), Flat 2, 34, Elgin-crescent, Notting Hill, W.
1904		Clayton, Ellis, Hazeldene, Deerpark-road, Belfast
1889		Clayton, John William, 3 and 5, Concert-street, Liverpool
1908		Clement, Leonard, M.A. (Cantab.), F.I.C., 11, Agnew-street, Lytham
1915	Trans.	Clemo, George Roger, B.Sc. (Lond.), 71, South Moor-road, Oxford
1875		Clerk, Dugald, Hon. D.Sc. (Manc.), F.R.S., 57 and 58, Lincoln's Inn-fields, W.C.
1916		Clifford, Percy Herbert, The Acacias, Hillingdon, Uxbridge
1914		Clifford, Sydney George, 51, Peak-hill, Sydenham, S.E.
1902		Clifford, William, Sewage Outfall Works, Wolverhampton
1913		Clotworthy, Harold Reginald Septimus, M.A. (Dub.), B.Sc. (Lond.), A.R.C.Sc.I., 6, Carrigfern, College-road, Cork, and Chemical Dept., University College, Cork
1878		Cloud, Thomas Charles, A.R.S.M., F.I.C., 479, Mansion House-chambers, E.C.
1907	Trans.	Clough, George William, B.Sc. (Birm.), Birkbeck College, Breams' Buildings, Chancery-lane, E.C.

Date of Election.			
1902			Clough, William Thomas, A.R.C.S., Chelladene, St. Margaret's-road, Wanstead Park, Essex
1869	Trans.	{C. 1885-90, 99-03}	‖Clowes, Frank, Prof., D.Sc. (Lond.), F.I.C., The Grange, College-road, Dulwich, S.E.
1902			Clowes, George Henry Alexander, Ph.D. (Göttingen), Gratwick Research Laboratory, The University, Buffalo, U.S.A.
1897			Clutterbuck, Medwin Caspar, B.Sc. (Lond.), Ph.D. (Strassburg), 61, Beaconsfield-villas, Brighton
1905	Trans.		Coates, Joseph Edward, M.Sc. (Wales), c/o T. Tyrer, Esq., Stirling Chemical Works, Abbey-lane, Stratford, E.
1887			Coates, William Henry, M.A., M.B. and L.S.A. (Dun.), M.R.C.S., L.R.C.P. and L.S.A. (Lond.), 7, Albion-street, Hull
1896			Cobb, Walter William, M.A. (Oxon.), Hilton House, Atherstone
1890			Cobbold, Paul Alexander, M.A. (Cantab.), Haileybury, Ontario, Canada
1895			Coblentz, Virgil, Prof., Ph.D. (Berlin), 23, Vine-street, Brooklyn, N.Y., U.S.A.
1880			‖Cockburn, Arthur Cecil, Torbay House, 156, Willesden-lane, N.W.
1906			Cockburn, Charles Taylor, 34, Queen's-gate, Dowanhill, Glasgow
1892			Cockerill, Thomas, Technical College, Colombo, Ceylon
1893			Cocking, Allan Thomas, Carhampton House, Four Oaks, Sutton Coldfield
1888			‖Cocking, Lewis Smith, Rashcliffe Dyewood Mills, Huddersfield
1902			Cockle, Charles, Belsay, Weeke-hill, Winchester
1910			Cocks, Reginald Henry, M.A. (Oxon.), The School House, Alresford, Hants.
1913			Cockshutt, John Albert, M.Sc. (Manc.), 27, Hornby-street, Oswaldtwistle, Accrington
1901			Coddington, Eustace, M.A. (Cantab.), St. John's School, Leatherhead
1903			Codling, Arthur John, 5, Tavistock-square, W.C.
1885	Trans.	C. 1908-12	Cohen, Julius Berend, Prof., Ph.D. (Munich), B.Sc. (Vict.), F.R.S., The University, Leeds; and 1, North Grange-mount, Headingley, Leeds
1914			Cohen, Lionel, Stock Department Laboratory, Casino, N.S.W.
1901			‖Cohen, Robert Waley, M.A. (Cantab.), 11, Sussex-square, W.
1912			Colclough, Tom Peach, M.Sc. (Manc.), Worksop-road, Handsworth, Sheffield
1913			Coleman, Herbert Stoddard, 3, Wyndham-road, Edgbaston, Birmingham
1883			Coleman, Joseph Bernard, F.I.C., S.W. Polytechnic Institute, Manresa-road, Chelsea, S.W.

Date of Election.			
1909			Coles, Alfred Bertram, M.A. (Oxon.), County Technical School, Workington
1910	Trans.		Colgate, Reginald Thomas, D.Sc. (Lond.), A.C.G.I., 25, Denmark-road, Reading
1883			Collenette, Adolphus, Brooklyn, Fort-road, Guernsey
1908			Collens, Archibald Edgar, Government Laboratory, Port of Spain, Trinidad
1905	Trans.		Colles, William Morris, jun., B.Sc. (Lond.), Chemical Laboratory, School of Medicine, Cairo, Egypt
1881			Collett, John Marton, Wynstone-place, Brookthorpe, Gloucester
1910			Collett, Ronald Leslie, M.A. (Cantab.), F.I.C., 21, Aubrey House, Maida Hill West, W.
1885	Trans.	C. 1889-94, 1900-1 V.P. 1909-12	‖Collie, John Norman, Prof., Ph.D. (Würzburg), Hon. D.Sc. (L'pool. and Belfast), F.R.S., F.I.C., 16, Campden-grove, Kensington, W.
1908	Proc.		Collier, William Henry, B.Sc. (Lond.), 13, Chatsworth-avenue, Wembley Hill, Middlesex
1897			Collingridge, Frank, B.Sc. (Lond.), F.I.C., Highstone, New-road, Llanelly
1911			Collington, John Eric, 11, Noel-road, Edgbaston, Birmingham
1892			‖Collins, Hugh Brown, Major, B.Sc. (Glas.), Auchinbothie Estate Office, Kilmacolm, Renfrewshire
1890			‖Collins, Sydney Hoare, M.Sc. (Dun.), F.I.C., 9, Cavendish-place, Newcastle-on-Tyne
1914			Collins, Stanley Winter, B.Sc. (Lond.), F.I.C., 33, Oakhill-court, East Putney, S.W.
1888			‖Collins, Walter Hepworth, Junior Constitutional Club, Piccadilly, W.
1887	Trans.	C. 1912-15	‖Colman, Harold Govett, D.Sc. (Vict.), Ph.D. (Würzburg), F.I.C., Woodthorpe, New Malden, Surrey
1915			Colverd, Owen, 52, Crofton-road, Plaistow, E.
1890			Colwell, James Kear, F.I.C., Clerkenwell Town Hall, Rosebery-avenue, E.C.
1900			Comber, Albert Walter, F.I.C., 23, Courtenay-gardens, Upminster, Essex
1892			‖Comyns, Frank, M.A. (Oxon.), Bryum, Craven-road, Newbury
1899			Connah, James, B.Sc. (Lond.), F.I.C., The Laboratory, Custom House, E.C.
1883			‖Conrad, Edwin Charles, H.M. Magazine, Thurmaston, Leicester
1906			Conyngham, William Boulton, 9, Belgrave-road, Monkstown, co. Dublin
1875	Trans.		‖Cook, Ernest Henry, D.Sc. (Lond.), F.I.C., The Clifton Laboratory, 27, Berkeley-square, Clifton, Bristol

Date of Election.		
1907		Cook, Taylor, B.Sc. (Lond.), A.R.C.S., Burgh Academy, Kilsyth, Glasgow
1911		Cooke, Charles Ernest, Oakdale, Eastwood-road, Woodford, E.
1916	Proc.	Cooke, John Harbourne, B.A. (Dub.), A.R.C.S.I., Dungarvan, co. Waterford
1888		Cooley, Walter Bromley, 5, Dudley-street, Wolverhampton
1912		Coombs, Frank Andrew, Technical College, Sydney, N.S.W.
1909		Coope, John Charles Jesser, Hillside, Bulawayo, Rhodesia, S. Africa
1898		‖Cooper, Albert John Bullen, 80, Gloucester-road, South Kensington, S.W.
1892		Cooper, Arthur James, B.A. (Dub.), B.Sc. (Lond.), F.I.C., Solihull School, Solihull, Birmingham
1908		Cooper, Charles Duncan, Fairview, Basildon, Billericay, Essex
1912		Cooper, Evelyn Ashley, D.Sc. (Lond.), Arborfield, Box Ridge-avenue, Purley, Surrey
1909		Cooper, George Stanley, B.Sc. (Lond.), A.K.C., Colwyn, Park-avenue, Castleford
1904		Cooper, Jabez Horace, B.A. (Oxon.), 10, Severn-street, Highfield, Leicester
1898		Cooper, John Burdon, M.D., B.S. and B.Sc. (Dun.), 12, The Circus, Bath
1910		Cooper, Leonard Harry, c/o Royal Crown Soap Co., Calgary, Alberta, Canada
1900	Trans.	Cooper, William Francis, B.A. (Cantab.), The Laboratory, Rickmansworth-road, Watford
1891		‖Cooper, Walter Johnson, The Elms, Lavernock, near Penarth
1894	Proc.	Coote, Arthur Herbert, B.Sc. (Lond.), 59, Foyle-road, Blackheath, S.E.
1899	Trans.	Cope, Frank, c/o Messrs. Graham & Cope, Ltd., Globe Mills, Dewsbury
1913	Trans.	Coppin, Noël Guilbert Stevenson, M.Sc. (Liv.), Beaconsfield, Higher Runcorn
1890		‖Coppock, John Bridgeford, B.Sc. (Lond.), F.I.C., Lee-lane, Horsforth, Leeds
1891	Trans.	Corbett, Charles Henry, The Avenue, Trowbridge, Wilts.
1888		‖Cornish, Vaughan, D.Sc. (Vict.), Woodville, Camberley
1906		Cornwall, Reginald de Vere, Medical and Public Health Dept., Salisbury, Rhodesia, S. Africa
1890		Corrie, David, Nobel's Explosives Co., West Quarter Factory, Polmont Station, Stirlingshire
1910		Coslett, Thomas Watts, Norman-road, Northfield, Birmingham

Date of Election.		
1893	Trans.	‖Coste, John Henry, F.I.C., Utopia, Gloucester-road, Teddington, Middlesex
1909		Couch, David Little, 88, Rue de Chezy, Neuilly-sur-Seine, Paris; and 59, Haig-road, Plaistow, E.
1892		‖Couldrey, Henry, c/o Messrs. Thos. Cook & Son, Ludgate-circus, E.C.
1914	Trans.	Coulthard, Albert, B.Sc. (Manc.), Ph.D. (Freiburg), 9, Portland-avenue, Stamford Hill, N.
1906	Trans.	Courtauld, Stephen Lewis, M.A. (Cantab.), 59, Pall Mall, S.W.
1900		‖Courtman, Ernest Owen, Denford House, Atkins-road, Clapham Park, S.W.
1903		‖Cousins, Francis George, B.Sc. (Lond.), 1, St. Cuthbert's-place, Durham
1901	Trans.	Cousins, Herbert Henry, M.A. (Oxon.), Government Laboratory, Kingston, Jamaica
1885		Cousins, William James, F.I.C., 47, Church-crescent, Muswell Hill, N.
1886	Trans.	‖Coutts, Francis James Henderson, M.D., B.Ch., B.Sc., and D.P.H. (Vict.), Rusland, Gloucester-road, Kingston Hill, Surrey
1910		Coventry, Bernard Okes, Imperial Forest Service, Dehra Dun, U.P., India
1908		Coverdale, Arthur Edward, 68, Broad-street, Worcester
1906	Trans.	Coward, Hubert Frank, D.Sc. (Manc.), Board of Education, Whitehall, S.W.
1898		Cowburn, Arthur William, 20, Mount-street, Manchester
1908		Cowburn, John Robert, 10, Eastwood-road, South Woodford, Essex
1882		‖Cowie, Thomas Rennie, Garnkirk House, Garnkirk
1905		Cowie, William Beaverly, 26, Clyde-street, Edinburgh
1908		Cowley, Robert Charles, College of Pharmacy, Brisbane, Queensland, Australia
1911		Cowling, Thomas, Chapel-street, Easingwold, Yorks.
1904		Cowper, Alfred Denys, B.Sc. (Lond.), Silvermere, Marina, Deal
1888		Cowper, Joseph, 50, King-street, Penrith
1898		Cox, Frederick Hudson-, F.I.C., 67, St. Thomas'-street, Weymouth
1904		Crabb, William, B.A. and B.Sc. (Lond.), 57, Edridge-road, Croydon
1870	Trans.	Crafts, James Mason, Prof., Ridgefield, Conn., U.S.A.
1914		Craig, Robert Barclay, 50, North Albion-street, Glasgow
1910		Cram, Marshall Perley, A.M. (Bowdoin), Ph.D. (Johns Hopkins), Bowdoin College, Brunswick, Maine, U.S.A.
1897		Cranfield, William, Daintree, Manor Court-avenue, Nuneaton

Date of Election.			
1910			Crawford, David Chalmers, M.A., B.Sc., and B.Sc. Agric. (Aberd.), Government College of Agriculture, Elsenburg, Mulders Vlei, Cape Colony, S. Africa
1909	Trans.		Creighton, Henry Jermain Maude, M.A. (Dalhousie), M.Sc. (Birm.), D.Sc. (Zürich), Assistant Professor of Chemistry, Swarthmore College, Swarthmore, Penn., U.S.A.
1914			Cremer, Herbert William, B.Sc. (Lond.), Preston Lea, Faversham
1914			Cresswick, John Arthur, Cress Dale, Villiers-street, Bexley, N.S.W., Australia
1909			Crewe, Philip Henry, Brynwood, Cromley-road, Davenport, Stockport
1887			‖Cribb, Cecil Howard, B.Sc. (Lond.), F.I.C., 60, Greek-street, Soho-square, W.
1910			Crichton, Charles, Kleinfontein Group, C.A., Box 2, Benoni, Transvaal, S. Africa
1878			‖Criper, William Risdon, A.R.S.M., F.I.C., Chemical Works, Konnagar, Calcutta, India
1906			Crocker, Henry Ernest, 50, Elgin-road, Seven Kings, Ilford
1902	Trans.		Crocker, James Codrington, M.A. (Cantab.), D.Sc. (Lond.), South Western Polytechnic, Manresa-road, Chelsea, S.W.; and 11, Lavengro-road, Dulwich, S.E.
1901			‖Crocker, Walter Stevens, A.R.C.S., 39, Arnold-street, Princes Park, Liverpool
1897	Trans.		Crofts, James Murray, M.A. (Cantab.), B.Sc. (Lond.), 24, Talbot-street, Southport
1886	Trans.		‖Crompton, Holland, Oaklyn, Cross Oak-road, Berkhamsted
1911			Crook, Clement Arthur, 5, Avondale-place, Manor-drive, Halifax
1857	Trans.	(C. 1866-70 V.P. 76-9, 85-7 P. 87-9)	‖Crookes, Sir William, O.M., D.Sc. (Oxon., R.U.I., Sheffield, Cape of Good Hope), Hon. LL.D. (Birm.), F.R.S., F.I.C., 7, Kensington Park-gardens, W.; and Athenæum Club, Pall Mall, S.W.
1879	Trans.	(C. 1890-1, 93-5, 1911-12)	‖Cross, Charles Frederick, B.Sc. (Lond.), F.I.C., 3, New-court, Carey-street, W.C.
1890	Trans.	(C. 1901-2 S. 1905-13 F.S. 1913-)	‖Crossley, Arthur William, Lt.-Col., D.Sc. (Vict.), Ph.D. (Würzburg), F.R.S., F.I.C., King's College, Strand, W.C.; and 46, Lindfield-gardens, Hampstead, N.W.
1896			Crossman, Charles Matthew, B.Sc. (Lond.), Cannon House, Watford, Herts.
1898			Crouch, William Samuel, c/o General Post Office, Perth, Western Australia
1880	Trans.		Crow, John Kent, D.Sc. (Lond.), F.I.C., Ivydene, Westcombe-park-road, Blackheath, S.E.

Date of Election.		
1887		‖Crowther, Horace Woodward, F.I.C., The Beeches, West Bromwich
1912		Crowther, Raymond Edwin, Westwood, Langford-road, Heaton Chapel, Stockport
1915		Crundall, Sydney Francis William, A.C.G.F.C., 28, Marlborough-hill, Harrow
1910	Trans.	Cumming, Alexander Charles, D.Sc. (Melbourne), 3, Gardiner-road, Blackhall, Midlothian
1914		Cunliffe, Harry, 7, Rinkvale Cottages, Hawick
1904		Cunningham, James Edward, Minas Peña del Hierro, Provincia del Huelva, Spain
1912		Curtis, Frederic Fernandez, 20, Bury-street, Bloomsbury, W.C.
1900		Cussons, John, B.Sc. (Vict.), P.O., Fauresmith, Orange Free State, S. Africa
1881		‖Custance, John D., Prof., Sherlock, S. Australia
1913		Cutbush, Charles George, 59, Byne-road, Sydenham, S.E.
1895		‖Cuthbertson, Lionel Mould Gurney, 89, Lordship Park, N.
1914		Cutler, John Vernell, c/o Messrs. E. W. Hawksworth and Sons, Beneva Estate, Esperanza, Natal, S. Africa
1911		Cutner, Morris, B.Sc. (Lond.), 28, Filey-street, Sheffield
1894		Dains, Herbert Henry, F.I.C., 7, Mount View-road, Crouch Hill, N.
1901	Trans.	Dakin, Henry Drysdale, D.Sc. (Vict.), F.I.C., 819, Madison-avenue, New York City, U.S.A.
1913		Dalal, Vasanji Premji, M.A. and B.Sc. (Bombay), Pension Scherrer, Heidelberg, Germany
1912		Dallas, William, Burnbank Cottage, Mount Vernon, Glasgow
1905		Dallman, Arthur Augustine, 17, Mount-road, Higher Tranmere, Birkenhead
1904		Dalton, William Herbert, 85, Hayter-road, Brixton Hill, S.W.
1887		Daniell, Louis Charles, Royal Standard Brewery, Tamworth, N.S.W.
1892	Trans.	Darbishire, Francis Vernon, B.A. (Oxon.), Ph.D. (Leipzig), Dorotheenstrasse 12, Dresden 20, Germany
1899		Darling, Charles Robert, A.R.C.S.I., F.I.C., 186, Eglinton-road, Plumstead, Kent
1891		Darling, Thomas, Adderstone House, Berwick-on-Tweed
1871	Trans.	‖Darling, William Howarth, F.I.C., 49, Oxford-road, Altrincham
1914		Das, Behari Lal, 107/2/1, Manaharpukur-road, Kalighah, Calcutta, India
1912		Das, Bhupati Nath, Prof., M.A. (Calcutta), B.Sc. (Lond.), Dacca College, Dacca, Eastern Bengal, India

Date of Election.		
1915		Das, Premananda, M.S. (Mich.), 72, Baranoshy Ghose-street, Calcutta, India
1911		Datta, Ganesh, B.A. (Punjab), Dera Ismail Khan, N.W.F.P., India
1914		Davenport, Sydney Edward, Fernbank, York-road, Windsor
1875		‖Davey, G. William, 22, Tubbs-road, Harlesden, N.W.
1905		Davey, Joseph Morgan, Shelone House, Briton Ferry, Glam.
1897		Davidge, Henry Norris, 11, Shaftesbury-avenue, W.
1900		Davidson, Alexander, jun., F.I.C., Whitecastle, Biggar
1906		Davidson, Charles, 24, Hamilton-drive, Cambuslang, Glasgow
1914		Davidson, Thomas Alexander, 57, Strathyre-avenue, Norbury, S.W.
1898	Trans.	Davidson, William Brown, M.A. and D.Sc. (Aberd.), Ph.D. (Würzburg), F.I.C., Hollinhurst, Kaffir-road, Edgerton, Huddersfield
1913		Davies, Daniel James, B.Sc. (Sheffield), 177, Le Marchant-road, St. John's, Newfoundland
1915		Davies, David Owen, 4, Victoria-avenue, Penarth
1913	Trans.	Davies, Harold, F.I.C., 18, Windsor-road, Ilford
1910	Trans.	Davies, John Hughes, B.Sc. (Wales), Ph.D. (Leipzig), 100, Park-road, Peterborough
1896		Davies, Llewellyn John, Bute-chambers, Bute-road, Cardiff
1894	Trans.	‖Davies, Samuel Henry, M.Sc. (Vict.), Messrs. Rowntree & Co., Ltd., York
1914		Davies, Thomas Eynon, B.Sc. (Wales), 31, Trevor-street, Aberdare
1915		Davies, Walter Thomas, B.A. and B.Sc. (Lond.), 3, Plant-street, Old Hill, Staffs.
1900		Davis, Arthur Charles, 4, Mount-avenue, Ealing, W.
1902		Davis, Charles Benson, National Brewers' Academy, 402, West 23rd-street, New York City, U.S.A.
1857		‖Davis, John Frederick, c/o Messrs. Herold & Gie, Temple-chambers, Wall-street, Cape Town, S. Africa
1876		‖Davis, Walter Charles, The Chestnuts, Durdham Down, Bristol
1897	Trans.	Davis, William Alfred, B.Sc. (Lond.), c/o Mrs. Lawrence, 102, Junction-road, Upper Holloway, N.
1900		Davison, Thomas Cuthbert, Bower-hill, Exmouth-street, Swindon
1906		Davson, Archibald Prideaux, A.R.C.S., F.I.C., 16, Airedale-road, South Ealing, W.
1912		Davys, Gerard Irvine, Major, I.M.S., B.A., M.D., B.Ch., and D.P.H. (Dub.), D.T.M. and H. (Cantab.), Beechview, Kidbrook-grove, Blackheath, S.E.
1916		Dawes, Cyril Stanley, 20, Glover-street, South Melbourne, Victoria, Australia

Date of Election			
1900	Trans.		Dawson, Harry Medforth, D.Sc. (Leeds), B.Sc. (Lond.), Ph.D. (Giessen), The University, Leeds; and 23, Claremont-drive, Headingley, Leeds
1909			Dawson, James Ferguson, B.Sc. (Manc.), Kirkhill, Penicuik, Midlothian
1881	Trans.		‖Day, Thomas Cuthbert, 36, Hillside-crescent, Edinburgh
1905			Day, William Walpole, B.Sc. (Wales), Malford, Lutterworth-road, Nuneaton
1912			De, Surendra Nath, L.M.S., 52, Brojanath Dutt-lane, Calcutta, India
1907			Dealy, Thomas Kirkman, Craigmin East, Cragmin-road, The Peak, Hong Kong
1901	Trans.		Dean, George, M.A. (Cantab.), 107, Earlham-grove, Forest Gate, E.
1916			Dean, Harry, Oak Villa, Greenbank-road, Huddersfield
1898	Trans.		‖De Castro, John Paul, M.A. (Cantab.), F.I.C., 1, Essex-court, Temple, E.C.
1869	Trans.		‖Deering, William Henry, I.S.O., F.I.C., Beauworth, Moreton-hampstead, Devon
1900	Proc.		Deerr, Noël Fielding, F.C.G.I., Granja Escuela, Cienaga, Havana, Cuba
1902			‖De la Rue, Sir Evelyn Andros, Bart., B.A. (Oxon.), 110, Bunhill-row, E.C.
1905			De Lury, Ralph Emerson, M.A. and Ph.D. (Toronto), The Dominion Astronomical Observatory, Ottawa, Canada
1911			Demuth, Rudolph, 68, Salusbury-road, N.W.
1907	Trans.		Denham, William Smith, D.Sc. (St. Andrews), B.Sc. (Lond.), F.I.C., Chiswick Laboratory, Church Wharf, The Mall, Chiswick, W.
1914			Denington, Richard Charles, A.I.C., 69, Dover-road, S. Wanstead, N.E.
1892			Denison, Joseph Richard, Messrs. J. R. Denison & Co., Valley Dyeworks, Bradford
1902			Dennis, William, Saxilby, Lincoln
1906			Denton, John, 86, Legrams-lane, Bradford
1903	Trans.		Desch, Cecil Henry, D.Sc. (Lond.), Ph.D. (Würzburg), F.I.C., Metallurgical Laboratory, The University, Glasgow
1870	Trans.	(C. 1874-7 / V.P. 80-3, 86-8, 96-7. / P. 97-9)	‖Dewar, Sir James, Prof., M.A. (Cantab.), Hon. LL.D. (St. Andrews, Aberd., Edin., Glas.), Hon. D.Sc. (Oxon., Dub., Vict., Ireland), Ph.D. (Christiania), F.R.S., F.I.C., Royal Institution, Albemarle-street, W.
1899			Dewhirst, John Arthur, F.I.C., The Borough Laboratory, George-square, Halifax

Date of Election.			
1916	Trans.		Dhar, Nilratan, Imperial College of Science and Technology S. Kensington, S.W.
1915			Dhavale, Bhaskar Balvant, M.A. (Bombay), 90, Idmiston-road, West Norwood, S.E.
1880			Dibdin, William Joseph, F.I.C., Chelton House, Burdon-lane, Belmont, Sutton
1912			Dick, Thomas Sharp, Stanley Villa, Broomberry-drive, Gourock, Renfrewshire
1908	Trans.		Dickinson, Cyril, B.Sc. (Vict. and Leeds), F.I.C., Southwark Town Hall, Walworth-road, S.E.
1898			Dickson, Samuel, Chemical Laboratory, 2, Broadway, Westminster, S.W.
1910	Trans.		Dickson, Thomas William, B.A. (Oxon.), c/o John Henderson, Esq., 60, Jeffrys-road, Clapham, S.W.
1906			Dickson, William, F.I.C., c/o Mrs. Orr, Endfield, Stevenston, Ayrshire
1912			Dieffenthaller, George Cruden, 10, Richmond-street, Port of Spain, Trinidad, B.W.I.
1907			Dikshit, Mohan Nath Kedarnath, Amliran, Surat, India
1906			Dinwoodie, James Herbert, 71, Bree-street, Johannesburg, S. Africa
1897			Dixon, Andrew James, F.I.C., Reiby Chambers, Reiby-lane, Circular Quay, Sydney, N.S.W.
1885	Trans.	C. 1900–06	Dixon, Augustus Edward, Prof., M.D. (Dub.), University College, and Fernhurst-avenue, Western-road, Cork
1896	Trans.		Dixon, Frank, B.Sc. (Lond.), The Institute, Lydney, Gloucester
1894	Proc.		‖Dixon, George, Lieut-Col., M.A. (Cantab.), Trinity College, Cambridge; and St. Bees, Cumberland
1876	Trans.	C. 1892-6 V.P. 1904-7 P. 1909-11	‖Dixon, Harold Baily, Prof., M.A. (Oxon.), Hon. Ph.D. (Prague), F.R.S., The University, Manchester; and 10, Wilbraham-road, Fallowfield, Manchester
1893			Dixon, Harry William, 3, Newton-road, Potternewton, Leeds
1912			Dixon, Walter Henry, 53, High-street, East Grinstead
1895			Dixon, William, 102, Spring-street, Bury
1862			Dixon, William Adam, F.I.C., Reiby Chambers, Reiby-lane, Circular Quay, Sydney, N.S.W.
1882	Trans.	C. 1901-6 V.P. 1907-11	Dobbie, Sir James Johnston, Prof., M.A. (Glas.), D.Sc. (Edin.) F.R.S., F.I.C., 4, Vicarage-gate, Kensington, W.
1887	Trans.		Dobbin, Leonard, Ph.D. (Würzburg), F.I.C., Chemical Laboratory, New University-buildings, Edinburgh
1916			Dobbs, Ernest John, 88A, East India-road, Poplar, E.
1910			Dodd, Alexander Scott, B.Sc. (Edin.), F.I.C., 173, Bruntsfield-place, Edinburgh
1910			Dodd, Arthur, Lyndhurst, Belvedere, Kent

Date of Election.			
1898			‖Dodd, Frederick Robertson, F.I.C., Welbank-villas, Liverpool-road, Aughton, Ormskirk
1901			Dodd, Robert, Birch Vale Cottage, Romiley, Stockport
1886			Dodd, William Ralph, Burton Grange, Goff's Oak, Waltham Cross
1912			Dodds, Herbert Henry, M.Sc. (Manc.), c/o Messrs. Kynoch, Ltd., Umbogintwini, Durban, Natal, S. Africa
1897	Trans.		Dodgson, John Wallis, B.Sc. (Lond.), University College, Reading
1912			Dodson, Harold Forster, 38, Steade-road, Nether Edge, Sheffield
1894	Proc.		Doherty, William Michael, F.I.C., Government Laboratory, Sydney, N.S.W.
1905			Donald, Robert, M.A. and B.Sc. (N.Z.), M.R.C.S. (Eng.), L.R.C.P. (Lond.), D.P.H. (Oxon.), Bacteriological Laboratory, The London Hospital Medical College, Turner-street, Mile End, E.
1892			Donaldson, Hudson, The Laurels, St. Catharine's - road, Grantham
1901	Trans.	C. 1913-4, 1915-	Donnan, Frederick George, Prof., M.A. (R.U.I.), Ph.D. (Leipzig), F.R.S., F.I.C., University College, Gower-street, W.C.
1897	Trans.		Dootson, Frederick William, M.A. (Cantab.), D.Sc. (Dub.), F.I.C., University Chemical Laboratory, Cambridge
1902	Trans.		‖Dorée, Charles, M.A. (Oxon.), D.Sc. (Lond.), 58, Gore-road, N.E.
1912			‖Douglas, James Crawford, Christmas Island Phosphates Co., Ltd., Christmas Island, Straits Settlements
1912			Douglas, Robert Percy, Prudential Buildings, Nelson-square, Bolton
1888			‖Douglas, William, F.I.C., Grafton House, Berkhamsted
1905			Doull, John, 22, Lauriston-place, Edinburgh
1913			Doumin, Roland, 76, Taunsfeld-road, Sydenham, S.E.
1911			Douse, Oliver Statham, M.Sc. (Manc.), Kia Ora, Compstall-road, Marple Bridge, Stockport.
1884			Down, Frederick Johnathan, Glengariff, Milton-road, Harpenden, Herts.
1916			Downie, James Russell, c/o Moreland Metal Co., Parramatta-road, Sydney, N.S.W.
1899			Doyle, Frederick, B.Sc. (Lond.), Higher Grade School, Carlisle
1913			Drakeley, Thomas James, B.Sc. (Lond.), The Mining and Technical College, Wigan
1884			Draper, Henry Carter, St. Kevin's, Sorrento-road, Dalkey, Co. Dublin
1891	Trans.		Dreaper, William Porter, F.I.C., 27, Willow-road, Hampstead, N.W.
1893			Dreyfus, Charles, Ph.D. (Strassburg), Claremont, Fallowfield, Manchester

Date of Election.		
1902		Drought, James Justinian, Molo, *vid* Mombasa, British East Africa
1915		Druce, John Gerald Frederick, Y.M.C.A., Tottenham Court-road, W.C.
1904	Trans.	Drugman, Julien, Ph.D. (Bonn), M.Sc. (Manc.), 117, Rue Gachard, Brussels
1913		Drummond, Jack Cecil, B.Sc. (Lond.), The Cancer Hospital Research Institute, Brompton, S.W.
1911		Dryden, Harold Edgar, The Laboratory, Messrs. S. Allsopp & Sons, Ltd., Burton-on-Trent
1897		Duckham, Alexander, Vanbrugh Castle, Blackheath, S.E.
1901		Duckworth, William Henry, Weaste House, Borough-road, Salford
1890		‖Dudley, William Lofland, Prof., Vanderbilt University, Nashville, Tenn., U.S.A.
1892		Duffield, Walter William, 5, Ashington-road, Hurlingham, Fulham, S.W.
1893	Trans.	‖Dufton, Samuel Felix, M.A. (Cantab.), D.Sc. (Lond.), Laurel Bank, Claremont-road, Headingley, Leeds
1884		Duggan, Thomas Richard, F.I.C., 52, East 41st-street, New York City, U.S.A.
1889		‖Dukes, Thomas William, P.O. Box 10, Vrijheid, S. Africa
1881		Duncan, Arthur William, c/o Messrs. Jas. Woolley, Sons & Co., Ltd., Victoria Bridge, Manchester
1894	Proc.	‖Duncan, Cecil Cooke, F.I.C., The Shire Hall, Worcester
1910		Duncan, James Hugh, 27, Richmond-road, Cardiff
1912		Duncan, John, 184, Pitt-street, Sydney, N.S.W.
1891		Duncan, William, F.I.C., The Laboratory, 65, Bath-row, Edgbaston, Birmingham
1896		Duncan, William, Royal Dispensary, 21, West Richmond-street, Edinburgh
1894	Proc.	‖Dunn, Frederic, 193, Collins-street, Melbourne, Australia
1909	Trans.	Dunn, Frederick Percy, B.Sc. (Lond.), 36, Lightwood-hill, Worley, near Birmingham
1882		Dunn, John Thomas, D.Sc. (Dun.), F.I.C., 10, Dean-street, Newcastle-on-Tyne
1908		Dunnicliff, Horace Barratt, Prof., M.A. (Cantab.), B.Sc. (Lond.), Khalsa College, Amritsar, Punjab, India
1909	Trans.	Dunningham, Alfred Charles, D.Sc. (Lond.), Ashville, Middlewich, Cheshire, and c/o Electro-Bleach and By-Products, Ltd., Middlewich, Cheshire
1893		Dunnington, Francis Perry, University of Virginia, Charlottesville, U.S.A.

Date of Election.			
1899			Dunscombe, Frederick Charles, c/o Electric Reduction Co., Buckingham, Quebec, Canada
1901	Trans.		Dunstan, Albert Ernest, D.Sc. (Lond.), East Ham Technical College, East Ham, E.
1885			Dunstan, Malcolm James Rowley, M.A. (Oxon.), F.I.C., The College, Wye, Ashford
1905			Dunstan, Sydney, The Royal Infirmary, Newcastle-on-Tyne
1879	Trans.	C. 1888-91 S.1893-03 V.P. 1903-06	‖Dunstan, Wyndham Rowland, Prof., C.M.G., Hon. M.A. (Oxon.), Hon. LL.D. (Aberd.), F.R.S., F.I.C., Imperial Institute, S.W.
1907			Dupré, Frederick Harold, St. Maur, Benhill Wood-road, Sutton Surrey
1907			Dupré, Percy Vivian, A.C.G.I., F.I.C., St. Maur, Benhill Wood-road, Sutton, Surrey
1906			Durrans, Thomas Harold, B.Sc. (Lond.), A.I.C., 10, Titchfield-terrace, North-gate, Regent's Park, N.W.
1883	Trans.		Durrant, Reginald Graham, M.A. (Oxon.), Rosetree, Marlborough
1911	Proc.		Dutt, Barum Chandra, Prof., M.A. (Calcutta), 172, Maniktola-street, Rambogan, Calcutta, India
1915	Trans.		Dutt, Pavitra Kumar, M.A. and B.Sc. (Calcutta), M.Sc. (Leeds), A.I.C., 16, Vernon-road, Leeds.
1912	Trans.		Dutta, Jatindra Mohan, M.A. (Calcutta), Dacca College, Dacca, Eastern Bengal, India
1892			Duxbury, Thomas, 17, Grosvenor-chambers, Deansgate, Manchester
1909			Dyche-Teague, Francis Clifford, B.Sc. (Birm.), F.I.C., 258, Gloucester-terrace, Hyde Park, W.
1875	Trans.	C 1893-7, 1904-08	‖Dyer, Bernard, D.Sc. (Lond.), F.I.C., 17, Great Tower-street, E.C.
1890	Trans.		Dymond, Thomas Southall, F.I.C., Board of Education, King Charles-street, Whitehall, S.W.
1912			Dyson, James Harry, 36, Prescott-street, Halifax
1883	Trans.		‖Dyson, Septimus, Nyddcombe, Warlingham, Whyteleafe, Surrey
1905			Eade, Samuel George, 35, Blackborough-road, Reigate
1911			Eardley, James Furnival, Woodside, Lindrick Common, near Worksop
1876			‖Earp, Francis Salsbury, Ph.D. (Giessen), F.I.C., 35, Porter-street, Kalgoorlie, W. Australia
1907			Eastaugh, Frederick Alldis, A.R.S.M., The University, Sydney, N.S.W.

Date of Election.		
1889	Trans.	‖Easterfield, Thomas Hill, Prof., M.A. (Cantab.), Ph.D. (Würzburg), F.I.C., Victoria University College, Wellington, New Zealand
1891		Eastick, Charles E., Martineau's Refinery, King Edward-street, Whitechapel, E.
1912		Eastick, Frederick Charles, B.A. (Cantab.), The Drive, South Woodford, N.E.
1881		‖Eastick, John Joseph, A.R.S.M., F.I.C., 2, St. Dunstan's-hill, E.C.
1908		Easton, Reginald Freeman, 111, Cromwell-road, St. Andrews, Bristol
1906		Eaton, Bertie James, F.I.C., Agricultural Dept., Kuala Lumpur, Selangor, Federated Malay States
1878	Trans.	‖Eccles, Herbert, Briton Ferry Steel Works, Briton Ferry, Glamorganshire
1909		Edgar, Edward Charles, Keithock, Marple Bridge, Stockport
1909		Edge, Alfred, Ravenhurst, Clayton Bridge, Manchester
1909		‖Edge, John Harold, Great Marld, Smithills, Bolton
1903	Proc.	Edgerton, John Percy, St. Lawrence House, 96, Cheapside, E.C.
1902	Trans.	Edminson, Sidney Robert, B.Sc. (Lond.), Preparatory School for Boys, Merchiston, Maritzburg, Natal, S. Africa
1913		Edmondson, James Henry, Southall-Norwood Sewage Purification Works, Wyke-green, Isleworth
1898		‖Edwards, Wilbraham Tollemache Arthur, M.R.A.C., F.I.C., Municipal Laboratory, Rose-hill, Mauritius
1909	Trans.	Egerton, Alfred Charles Glyn, B.Sc. (Lond.), 19, Old Court Mansions, W.
1911		Eggington, Alfred Thomas, B.Sc. (Lond.), A.R.C.S., Borlase School, Marlow
1887		‖Ehrhardt, Ernest Francis, D.Sc. (Lond.), Ph.D. (Munich), B.Sc. (Birm.), Mersey Chemical Works, Bromborough Port, Birkenhead
1913		Eldin, Mohamed Shamo, B.Sc. (Manc.), School of Medicine, Cairo, Egypt
1911		Eldridge, Arthur Alfred, B.Sc. (Lond.), F.I.C., 63, Ellerton-road, Surbiton Hill, Surbiton, BO., Surrey
1907		Elias, Owen Aubrey, 123, Waller-road, New Cross, S.E.
1878	Trans.	‖Elliott, Arthur Henry, Ph.D. (Columbia), The Chemists' Club, 52, East 41st street, and The College of Pharmacy, 115, West 68th-street, New York City, U.S.A.
1913		Elliott, Thomas Lenton, c/o The Straits Trading Co., Ltd., Singapore, Straits Settlements
1893		Ellis, Charles Sordes, F.I.C., The Authors' Club, 2, Whitehall-court, S.W.

Date of Election.		
1900		Ellis, Frederic Richard, 28, Seymour-road, Ashley Down, Bristol; and 99, Cambridge-street, Warwick-square, S.W.
1903	Proc.	Ellis, Henry Russel, B.Sc. (Lond.), Lakeside, Staines
1912		Ellis, Ridsdale, B.Sc. (Boston), 1626, Lytton-building, Chicago, Ill., U.S.A.
1912		Ellis, Rowland Holliday, F.I.C., Lynwood, Thorpe-road, Selby
1892		Ellison, Henry, jun., Whitechapel-road, Cleckheaton
1893		Elmore, Alexander Stanley, 72, Gloucester-terrace, Hyde Park, W.
1902	Trans.	Elsden, Alfred Vincent, B.Sc. (Lond.), F.I.C., Chemical Department, Royal Arsenal, Woolwich, S.E.
1912		Elsdon, George Davidson, B.Sc. (Birm.), F.I.C., Municipal Laboratory, 141, Regent-road, Salford
1885		Embrey, George, F.I.C., City and County Laboratory, 47, Park-road, Gloucester
1911		Emerson, Robert Leonard, A.B. and M.D. (Harvard), 1808, Eye-street, N.W., Washington, D.C., U.S.A.
1910	Trans.	Emmett, William Gidley, M.A. (Cantab.), Broadgate, Beeston, Nottingham
1887		‖Emmons, Hamilton, The Copse, Hamble, Southampton
1911		Empson, Alfred Walker, A.M.I.E.E., A.M.I.Mech.E., 14, Scarcroft-hill, York
1901		English, Robert, Christchurch Gas Co., Christchurch, New Zealand
1914		Ennos, Frederick Raine, B.A. (Cantab.), B.Sc. (Lond.), 50, Culverley-road, Catford, S.E.
1916		Ensoll, Robert, 148, Devonshire-avenue, Southsea
1892		Entwistle, Herbert, Fairholme, Redclyffe-road, Palatine-road, Manchester
1899		Epps, James Washington, c/o Messrs. James Epps & Co., Ltd., Holland-street, Blackfriars, S.E.
1889		Erskine, James Kerr, New Kleinfontein Co., Ltd., Post Office, Benoni, Transvaal, S. Africa
1915		Essery, Reginald Ernest, B.Sc. (Bristol), 24, Osterley Park-road, Southall, W.
1865		‖Estcourt, Charles, F.I.C., Seymour House, Seymour-grove, Old Trafford, Manchester
1899		‖Estcourt, Harry Estcourt, 467, West-street, Durban, Natal, S. Africa
1888		‖Estcourt, Philip Anderson, F.I.C., Seymour House, Seymour-grove, Old Trafford, Manchester
1894		Eumorfopoulos, Nicholas, B.Sc. (Lond.), 24, Pembridge-gardens, W.
1904		Evans, Edward Victor, F.I.C., The Laboratory, South Metropolitan Gas Co., 709, Old Kent-road, S.E.

Date of Election		
1912		Evans, Elliott Alfred, c/o Messrs. C. C. Wakefield & Co., Wakefield House, Cheapside, E.C.
1891		Evans, Frederick Arthur, c/o Messrs. King & Co., 58, Toop-street, Cape Town, S. Africa
1906		Evans, Frederick Watkins, Medical Hall, Cwmfelinfach, Newport, Mon.
1915		Evans, Henry Jackson, B.Sc. (Lond.), Taormina, Burdon Lane, Cheam, Sutton
1904		Evans, John, F.I.C., 67, Surrey-street, Sheffield
1892	Trans.	‖Evans, Robert Cecil Turle, M.B. and B.S. (Lond.), M.R.C.S. (Eng.), L.R.C.P., L.S.A., D.P.H. and B.Sc. (Lond.), Sandringham House, Marine-crescent, Herne Bay, Kent
1913		‖Evans, Ulick Richardson, B.A. (Cantab.), The Keir, The Common, Wimbledon, S.W.
1888		‖Everard, Arthur George, 43, Clapham-road, S.W.
1910	Trans.	Everest, Arthur Ernest, D.Sc. (Birm.), Ph.D. (Bâle), Department of Coal Tar Colour Chemistry, Technical College, Huddersfield
1902		Everitt, Walter, Norwood Wharf, Southall, Middlesex
1896	Trans	Ewan, Thomas, M.Sc. (Vict.), Ph.D. (Munich), c/o Cassel Cyanide Co., Ltd., Shuna-street, Maryhill, Glasgow
1909	Trans.	Ewins, Arthur James, D.Sc. (Lond.), 141, Woodwarde-road, Dulwich, S.E.
1902	Trans.	Eynon, Lewis, B.Sc. (Lond.), F.I.C., 4, Stag-lane, Buckhurst Hill, Essex.
1901	Trans	Eyre, John Vargas, Ph.D. (Leipzig), South Eastern Agricultural College, Wye, Ashford
1888		Faber, Harald Nicolai, 7 and 8, Idol-lane, E.C.
1904		Fagan, Thomas Wallace, M.A. (Cantab.), Edinburgh and East of Scotland College of Agriculture, 13, George-square, Edinburgh
1916		Fairbrother, Fred, B.Sc. (Manc.), 8, Benfield-street, Heywood
1865	Trans.	‖Fairley, Thomas, F.I.C., 17, East-parade, Leeds
1899		Fairweather, Ernest Barratt, King's College Hospital, Denmark Hill, S.E.
1908		Fairweather, James Hill, Chemical Laboratory, Brentford Gas Co., High-street, Brentford
1908		Falk, Kaufman George, B.Sc. (Columbia), Ph.D. (Strassburg), 151, Central-park-west, New York City, U.S.A.
1915	Trans.	Fargher, Robert George, M.Sc. (Manc.), 34, Myddelton-square, E.C.
1888		Farlie, John Burke, 2, Tirlemont-road, South Croydon
1912		Farlie, John Burke, jun., c/o British Post Office, Constantinople, Turkey

Date of Election			
1906			Farmer, Charles George Edgar, 4, Brick-court, Temple, E.C.
1903	Trans.		Farmer, Robert Crosbie, D.Sc. (L'pool.), Ph.D. (Würzburg), F.I.C., 42, Heriot-road, Hendon, N.W.
1895			Farr, Edward Henry, Uckfield, Sussex
1870			‖Farries, Thomas, F.I.C., 12, Coleman-street, E.C.
1880			‖Farrington, Thomas, M.A. (Q.U.I.), F.I.C., 4, Waterloo-place, Cork
1903	Trans.		Fawsitt, Charles Edward, Prof., D.Sc. (Edin.), Ph.D. (Leipzig), The University, Sydney, N.S.W.
1897	Trans.		Fenby, Alarick Vincent Colpoys, B.Sc. (Lond.), 45, Culmstock-road, Clapham Common, S.W.
1878	Trans.	(C. 1898-1902)	‖Fenton, Henry John Horstman, M.A. and Sc.D. (Cantab.), F.R.S., F.I.C., Christ's College, and 19, Brookside, Cambridge
1914			Ferguson, James, c/o Messrs. Brotherton & Co., Ltd., Tar Works, Stourton, Leeds
1872		C. 1889-93	‖Ferguson, John, Prof., M.A. (Glas.), LL.D. (St. Andrews), F.I.C., The University, Glasgow
1916			Ferguson, Robert, c/o Messrs. Blundell Spence & Co., Ltd., Beverley-road, Hull
1912			Fergusson, Donald MacEachern, c/o Acadia Sugar Refining Co., Ltd., Halifax, Nova Scotia
1899			Fermor, Herbert Frederick Francis Burdett, 32, Trossacks-road, East Dulwich, S.E.
1914			Fernie, Charles George, B.Sc. (Lond.), West Wratting Park, West Wratting, Cambridge
1909	Trans.		‖Ferraboschi, Frederic, M.A. (Cantab.), 21, Lawrie-park-road, Sydenham, S.E.
1902			Ferrand, Frederick, Wicken Cottage, Manchester-road, Heywood
1882			Ferrier, James, P.O. Box 764, Rome, Georgia, U.S.A.
1902			Ferris, Percy James, Rokeby-street, Collingwood, Melbourne, Australia
1906			Field, Samuel, A.R.C.S., Northampton Polytechnic Institute, Clerkenwell, E.C.
1904			Field, William Eddington, Martin-street, Elsternwick, Melbourne, Australia
1911			Fielding, Michael Angelo, Holm Lea, Ballintemple, Cork
1895			‖Fielding, Patrick Joseph Dominick, Rovigo, Victoria-road, Cork
1900	Trans.		Findlay, Alexander, Prof., M.A. and D.Sc. (Aberd.), Ph.D. (Leipzig), F.I.C., University College of Wales, Aberystwyth
1908			Findley, Albert Edward, B.Sc. (Birm.), Dept. of Applied Science, The University, St. George's-square, Sheffield
1910			Finlayson, John George, B.A. (Cantab.), 19, Westoe-parade, South Shields
1904			Finlow, Robert Steel, B.Sc. (Wales), F.I.C., Dacca, Bengal, India

Date of Election.			
1905	Trans.		Finnemore, Horace, B.Sc. (Lond.), F.I.C., Guy's Hospital, S.E.
1896			Fisher, Ernest Hunter, The County Laboratory, St. Albans
1872	Trans.		‖Fisher, Walter William, M.A. (Oxon.), F.I.C., 5, St. Margaret's-road, Oxford
1873			Fison, Edward Herbert, Stoke House, Ipswich
1906			Fitzgerald, Anthony Nisbet, B.A. and B.Sc. (Lond.), 1, King's-parade, Muswell Hill, N.
1914	Trans.		Fleck, Alexander, B.Sc. (Glas.), Radiometric Laboratory, Chemistry Department, The University, Glasgow.
1896			Fleet, John Thomas, 24, Sheep-street, Rugby
1912			Fleet, Wilfrid James, Imatra, King's-road, Bournemouth
1898			‖Fleming, John Arnold, 5, Windsor-terrace, Glasgow, W.
1874			Fletcher, Frederick William, North London Chemical Works, Holloway, N. ; and Beauchamp Lodge, Enfield
1885		C. 1893-4	‖Fletcher, Sir Lazarus, M.A. (Oxon.), Hon. LL.D. (St. Andrew's), Hon. Ph.D. (Berlin), F.R.S., Natural History Museum, Cromwell-road, S.W. ; and 35, Woodville-gardens, Ealing, W.
1894			‖Flintoff, Robert John, Gale, Cardigan-road, Bridlington
1892			Floris, Robert Brooke, F.I.C., Heathwood, Woodside-road, Beaconsfield, Bucks.
1906	Trans.		Flürscheim, Bernhard, Ph.D. (Heidelberg), Rushmoor, Fleet, Hants.
1894			Fogg, Charles Albert, Graythorne, Albert-road, Bolton
1859			Fogg, Thomas, 93, Portsdown-road, Maida Vale, W.
1889			Foggie, John, University College, Dundee
1902			Foll, Edgar, The Cottage, The Lion Brewery, Belvedere-road, Lambeth, S.E.
1885			Follows, Harold, 5, Kedleston-avenue, Victoria-park, Manchester
1894			‖Forbes, Donald Gordon, Shillingstone, Blandford
1915			Forbester, Robert Edward, M.Sc. (Dun.), Lyndhurst, Causeway Green-road, Langley Green, Birmingham
1889	Trans.		Ford, John Simpson, c/o Messrs. W. Younger and Co., Abbey Brewery, Edinburgh
1907			Foreman, Charles Thomas, Jamalpur, East Indian Railway, Bengal, India
1886			Formoy, James Arthur, 5, Willoughby-road, Hampstead, N.W.
1904			Forrest, John Kerr, Brae Lea, Austen-road, Guildford
1909			Forrester, George Peters, 69, Beckstrasse, Darmstadt, Germany
1909			Forshaw, Arthur, M.Sc. (Manc.), Essex Works, Aston, Birmingham
1892	Trans.	C. 1901-04 S. 1904-10 V.P. 1910-13. T. 1915—	†‖Forster, Martin Onslow, D.Sc. (Lond.), Ph.D. (Würzburg), F.R.S., F.I.C., Queen Anne's Mansions, St. James' Park, S.W.

† Longstaff Medallist, 1915.

Date of Election.			
1916	Trans.		‖Forster, Robert Benjamin, Ph.D. (Berlin), A.R.C.Sc.I., c/o Messrs. Levinstein, Ltd., Blackley, Manchester
1903			Forster, William, 30, Church-street, Seaham Harbour
1912			Foster, Alfred George Ernest, 103, St. Mark's-road, Easton, Bristol
1856	Trans.	C. 1865-8. 72-5, 85-6. V.P. 88-92.	‖Foster, George Carey, B.A. (Lond.), LL.D. (Glas.), D.Sc. (Vict.), F.R.S., Emeritus Professor of Physics, University College, Gower-street, W.C.; and Ladywalk, Rickmansworth, Herts.
1872			Foster, Reginald Le Neve, Fulshaw Cottage, Wilmslow, Manchester
1900			Foulds, James, A.R.C.S., Hollyhurst, Granville-road, Bold Venture-park, Darwen
1914	Trans.		Foulds, Robinson Percy, M.Sc. (Manc.), Stanley Villa, Colne
1898			Foulerton, Alexander Grant Russell, F.R.C.S. (Eng.), L.R.C.P. (Lond.), D.P.H. (Cantab.), 1, Morpeth-terrace, Victoria-street, S.W.
1891	Trans.		‖Fowler, Gilbert John, D.Sc. (Vict.), F.I.C., The Frankland Laboratory, The University, Manchester, and Indian Institute of Science, Bangalore, India
1900			Fowler, Morris Broad, 19, Westbury-road, Westbury-on-Trym, Bristol
1882			‖Fowler, William, 78, Melton-terrace, New Hartley, Seaton Delaval, Northumberland
1909			Fowler, William, 2, Gloucester-terrace, Barking-road, E. Ham, E.
1907	Trans.		Fowles, George, B.Sc. (Lond.), 79, Speldhurst-road, Bedford Park, W.
1895			Fox, Albert Stanley, Courtenay Lodge, Sutton Courtney, Abingdon
1907	Trans.		Fox, John Jacob, D.Sc. (Lond.), 6, Alkham-road, Stamford Hill, N.
1907			Foxell, Edward William Lanchester, B.Sc. (Lond.), Barnes, Christ's Hospital, West Horsham, Sussex
1916			Foxwell, Geoffrey Edwin, Carnock Colliery, Cowie, Bannockburn, Stirlingshire
1906			Foy, Peter Bertram, 16, Burlington-road, Dublin
1909	Trans.		Francis, Arthur Gordon, B.Sc. (Lond.), F.I.C., The Government Laboratory, Clement's Inn Passage, Strand, W.C.
1879			Francis, Edward, Clifton-lane, Ruddington, Nottingham
1902	Trans.		Francis, Francis Ernest, Prof., D.Sc. (Vict.), Ph.D. (Erlangen), F.I.C., The University, Bristol
1873			‖Francis, George Bult, 22-30, Graham-street, City-road, N.
1912	Trans.		Frankland, Edward Percy, B.A. (Cantab.), Ph.D. (Würzburg), M.Sc. (Birm.), Needlehouse, Ravenstonedale, Westmoreland

Date of Election.			
1881			Frankland, Henry, F.I.C., Streonshalh, The Crescent, Linthorpe, Middlesbro'.
1880	Trans.	C. 1887-9 V.P. 1902-05. P. 1911-13.	‖Frankland, Percy Faraday, Prof., Hon. LL.D. (St. Andrews), Hon.Sc.D. (Dub.), Ph.D. (Würzburg), Hon. M.Sc. (Birm.), B.Sc. (Lond.), A.R.S.M., F.R.S., F.I.C., The University, Birmingham ; and The Dell, Northfield, Birmingham
1915			Fraser, James, 44, Cumballa-hill, Bombay, India
1892			‖Fraser, James Christopher, Austin-street, Adelaide, S. Australia
1909			Fraymouth, William Adolf, Eastern States of Central India Export Trust, Esociet, Maihar, E.I.R., India
1887			Freeman, Frederick William, Heatherdale, Arden-grove, Harpenden, Herts.
1913			Freeman, Horace, c/o Dominion of Canada Assay Office, P.O. Box 804, Vancouver, British Columbia
1900			Freeman, Willie Ludford, M.A. (Oxon. and Dub.), LL.D. (Dub.), The Education Offices, Stoke-on-Trent
1889			Freestone, Joseph Thomas, Limehurst, Plymyard-avenue, Bromboro', Birkenhead
1892	Proc.		French, William, M.A. (Cantab.), F.I.C., Wheatfield, Lancaster
1903	Trans.		Friend, John Albert Newton, D.Sc. (Birm.), Ph.D. (Würzburg), F.I.C., The Victoria Institute, Sansome-walk, Worcester
1890			‖Frost, Robert, B.Sc. (Lond. and Vict.), 55, Kensington-court, Kensington, W.
1904			‖Fry, George, Carlin Brae, Berwick-on-Tweed
1899	Trans.		Frye, Colin Charlwood, F.I.C., 18, Woodfield-road, Ealing, W.
1880			‖Fryer, Alfred Cooper, M.A. and Ph.D. (Leipzig), F.I.C., 13, Eaton-crescent, Clifton, Bristol
1907			Fryer, Percival John, Ravenscar, Pembury-road, Tonbridge
1891			Fulcher, Lionel William, B.Sc. (Lond.), The Science College, S. Kensington, S.W., and Lisden, London-road, Norbury, S.W.
1896			Fuller, Charles James Pemeller, 603, Chorley-new-road, Horwich, Lancs.
1913			Fuller, Cyril Duncan, c/o Messrs. Aspinall's, Ltd., New Cross, S.E.
1909			Furneaux, George Pomeroy, M.A. (Oxon.), 47, Mount Pleasant-road, Hastings
1914	Trans.		Furness, Reginald, M.Sc. (Vict.), Cramwell, Walton New-road, Stockton Heath, Warrington
1906	Proc.		Fyleman, Martin Ernest, B.Sc. (Lond.), Ph.D. (Bâle), F.I.C., c/o The Osram Lamp Works, Ltd., Brook-green, Hammersmith, W.

Date of Election.		
1894		‖Gabb, George Hugh, 83, Crayford-road, Tufnell Park, N.
1899		Gabriel, Edmund Vivian, C.S.I., C.V.O., M.A. (Cantab.), Babbacombe Glen, Babbacombe, Torquay
1901		Gadd, Henry Wippell, Barrister-at-Law, 100, Fore-street, Exeter
1912		Gadd, Sydney Charles, 42, Velwell-road, Exeter
1913		Gair, Charles John Dickenson, 39, Cranston-road, Forest Hill, S.E.
1912		Gajjar, Madanlal Jekisandas, M.A. (Bombay), Girgaum Chemical Laboratory, Standhurst-road, Bombay, India
1901		‖Gajjar, Tribhuvandas Kalyandas, Prof., M.A. and B.Sc. (Bombay), Girgaum, Bombay, India
1905		Gall, John Beaconsfield, A.C.G.I., F.I.C., 49, Glenlyon-road, Eltham Park, Kent
1912		Gallogly, Michael Francis, Rev. Prof., B.A. (R.U.I.), St. Colman's College, Newry
1911		Gallsworthy, Benjamin, c/o The Gulf Refinery Co., Port Arthur, Texas, U.S.A.
1914		Galt, Hugh Miller, B.Sc. and M.B. (Glas.), D.P.H. (Cantab.), Elmcroft, Withdean, Brighton
1915		Gandhi, Nagardas Purushottam, M.A. and B.Sc. (Bombay), A.R.S.M., D.I.C., c/o Messrs. Tata Sons & Co., Tavoy, Burma
1908	Trans.	Ganguli, Atul Chandra, Prof., B.A. (Calcutta), Ravenshaw College, Cuttack, Orissa, India
1912		Garbutt, Cornelius Durham, 44, Long-lane, Garston, Liverpool
1883	Proc.	‖Garbutt, Llewellyn, M.A. (Cantab.), The College, Winchester
1909		‖Gardiner, Alexander David, 6, Wellfield-terrace, Springburn, Glasgow
1888		Gardiner, James Henry, 59, Wroughton-road, Balham, S.W.
1905		Gardner, Charles Richard, Chemical Laboratory, Gathurst, Wigan
1906		Gardner, Edward, Bigwood-road, Meadway, Hendon, N.W.
1909	Trans.	‖Gardner, Henry Dent, M.Sc. (Manc.), 46, The Goffs, Eastbourne
1893	Trans.	Gardner, John Addyman, M.A. (Oxon.), F.I.C., Chemical Department, St. George's Hospital, S.W.
1888	Trans.	Gardner, Walter Myers, Prof., M.Sc. (Leeds), F.I.C., Technical College, Bradford; and 3, Fairmount, Manningham, Bradford
1911		Gardner, William Temple, 14, Beechwood-avenue, Kew Gardens, BO., Surrey
1911		Gardthausen, Charles Christian, P.O. Box 80, Mines Dept., Geological Survey Office, Pretoria, Transvaal, S. Africa
1910	Trans.	Garland, Charles Samuel, B.Sc. (Lond.), A.R.C.S., A.I.C., 57, Garratt-lane, Wandsworth, S.W.
1913		Garland, Herbert, P.O. Box 417, Cairo, Egypt
1911		Garner, John Henry, B.Sc. (Lond.), Sewage Works, Deighton, Huddersfield

Date of Election.		
1916	Trans.	Garner, William Edward, M.Sc. (Birm.), 200, Burrage-road, Woolwich, S.E.
1893	Trans.	Garnett, Henry, 309, Oxford-road, Manchester
1913		Garrett, Albert Edward, B.Sc. (Lond.), c/o Dr. Jaeger's Co., Ltd., 95, Milton-street, E.C.
1889	Trans.	Garrett, Frederic Charles, D.Sc. (Vict.), 27, Fern-avenue, Newcastle-on-Tyne
1898		Garside, Arthur Leonard Harry, c/o Dr. A. K. Miller, F.I.C., 19, Kilvert's Buildings, Withy-grove, Manchester
1914		Garth, John, L.R.C.P. I. and L.M., 170, St. Thomas's-road, Preston
1906		Garvey, Richard Godfrey Hamilton, 5, Ellington-road, Muswell Hill, N.
1884		Gaskell, Joseph, 71, Haworth's-buildings, Cross-street, Manchester
1900		Gasson, William, Dutoitspan-road, Kimberley, S. Africa
1903		Gatehouse, Frank Brooks, Maristowe, Butts Green-road, Hornchurch, Romford
1911	Trans.	Gauge, Arthur Josiah Hoffmeister, 8, Hazelwood-villas, Hazelwood-lane, Palmer's Green, N.
1912		Gaul, Ernest George, M.Sc. (Manc.), The College, Holmes Chapel, Cheshire
1911		Gaunt, Rufus, M.Sc. (Leeds), Ph.D. (Berlin), 1, Beech-grove, Fountain-street, Morley, Leeds
1904	Trans.	Gawler, Robert, M.Sc. (Vict.), F.I.C., Central Technical School, Leeds Institute, Leeds
1887		Geisler, Joseph Frank, Mercantile Exchange Buildings, Hudson and Harrison-streets, New York City, U.S.A.
1885		Gemmell, George Harrison, F.I.C., 4, Lindsay-place, Edinburgh
1903		Gent, Percy William, Trentholme, Misterton, Gainsboro'
1879		‖Gent, William Thomas, Misterton, Gainsboro'
1914		George, Ernest, B.A. (Cape Univ.), Victoria-square, King William's Town, S. Africa
1896		George, George, F.I.C., Director of Technical Instruction, Auckland, New Zealand
1889		‖Gerland, Conrad, M.Sc. (Vict.), Ph.D. (Marburg), Meadow Bank, Accrington
1891		German, George, jun., Mansion House, Ashby-de-la-Zouch
1895		‖Gerrans, Henry Tresawna, M.A. (Oxon.), 20, St. John-street, Oxford
1875		Gerrard, Alfred William, Southmead, St. Agnes-road, Moseley, Birmingham
1899		Getman, Frederick Hutton, Ph.D. (Johns Hopkins), Hillside Laboratory, Glenbrook-road, Stamford, Conn., U.S.A.

Date of Election.		
1904		Ghose, Anu, 42, Shambazar-street, Calcutta, India
1911		Ghose, Joges Chandra, Prof., M.A. (Calcutta), Jagannath College, Dacca, Bengal, India
1913		Ghose, Tin Kari, B.A. and L.M.S. (Calcutta), 23/1, Baniatola-street, Hatkhola P.O., Calcutta, India
1914	Trans.	Ghosh, Brojendranath, M.Sc. (Calcutta), 19, Tavistock-road, Bayswater, W.
1912		Ghosh, Jyotish Chandra, B.Sc. (Manc.), Gov't. Medical Stores, Mint Buildings, Madras, India
1915		Ghosh, Sudhamoy, D.Sc. (Edin.), M.Sc. (Calcutta), 45, Rupnarayan Nandan-lane, Bhowanipur, Calcutta, India
1890		‖Gibbes, Cuthbert Chapman, M.D. and C.M. (Aberd.), M.R.C.P. (Lond.), D.P.H. (Cantab.), 89, Harley-street, Cavendish-square, W.
1900		Gibbings, George William, c/o Standard Bank of South Africa, Salisbury, Rhodesia, S. Africa
1912		Gibbins, Richard Ernest, 49, Park-road, Coventry
1897		Gibbons, Joseph Lake, Secondary School, Blyth, Northumberland
1907	Trans.	Gibson, Charles Stanley, Prof., M.A. (Oxon. and Cantab.), B.Sc. (Oxon.), M.Sc. (Manc.), The University Chemical Laboratory, Cambridge
1900		Gibson, John, 18, Fore-street, Hexham
1913		Gibson, Stanton, B.Sc. (Lond.), 28, Lordship-park, N.
1907		Gibson, William Howieson, B.Sc. (Lond.), Beaumond Lodge, King Edward-road, New Barnet, BO., Herts.
1888		Gibson, William Humphrey, 122, King's-road, Brighton
1911		Giddy, Thomas Grantham, Kenilworth, Samdon-street, Hamilton, N.S.W.
1895		Gilbard, John Francis Hutchins, F.I.C., 245, Dalston-lane, Hackney, N.E.
1904		Gilchrist, James Gray, M.A. (Aberd.), B.Sc. (Lond.), Blythswood, Victoria-road, Annan
1898		Gilderdale, Frederick, 32, Treherne-road, High West Jesmond, Newcastle-on-Tyne
1883		‖Gill, Ernest Clarendon, 10, Barrack-road, Christchurch
1902		Gill, J. Arthur, Pennsylvania, Lower-green-road, Rusthall, Tunbridge Wells
1916		Gill, John Henry, 16, Premier-road, Nottingham
1898	Proc.	Gilles, William Setten, A.C.G.I., F.I.C., The Cottage, Bocking, Braintree, Essex
1908	Trans.	‖Gilling, Charles, B.Sc. (Lond.), A.I.C., 9, Alwyne Mansions, Wimbledon, S.W.

Date of Election		
1916		Gilmour, George van Barneveld, B.Sc. (Lond.), A.R.C.S.I., The Laboratory, Maypole Margarine Works, Ltd., Southall
1913	Trans.	Gilmour, Robert, Ph.D. (Würzburg), B.Sc. (St. Andrews), 40, Ulsterville-avenue, Belfast
1908	Proc.	Girvan, Arthur Frank, B.Sc. (Lond.), Staffa, The Avenue, Gipsy Hill, S.E.
1914	Trans.	Gittins, James Mylam, M.Sc. (Wales), The Grammar School, Folkestone
1898		Glaister, John, Prof., M.D. (Glas.), M.R.C.S. and L.R.C.P. (Edin.), 18, Woodside-place, Glasgow
1907		Gledhill, Walter George, M.A. (Cantab.), The School House, Woodbridge
1912		Glegg, Robert, B.Sc. (Aberd.), F.I.C., 19, Mount-street, Aberdeen
1913		Glenday, Roy Gonçalves, B.A. (Cantab.), The Magadi Soda Co., Ltd., Magadi, British East Africa
1872		‖Glover, George Thomas, F.I.C., 63, St. James-street, Pall Mall, S.W., and Lowood, Hindhead, Surrey
1904		Glover, Harry James, St. Katharine's, Westham, Pevensey, Hastings
1906	Trans.	Glover, Walter Hamis, Ph.D. (Leipzig), 28, St. Paul's-road, Coventry
1907	Trans.	Godden, William, B.Sc. (Lond.), A.R.C.S., F.I.C., Agricultural Department, The University, Leeds
1910		Goddon, George Alexander, 18, Rylett-crescent, Shepherd's Bush, W.
1899		Golding, John, F.I.C., University College, Reading
1910		Goldsbrough, Harold Albert, F.I.C., c/o Dr. P. Schidrowitz, 57, Chancery-lane, W.C.
1878		‖Goldschmidt, Samuel Anthony, A.M. (C.C.N.Y.), E.M. (Columbia), Ph.D. (Emory Coll.), 11, Broadway, New York City, U.S.A.
1889		Goldsmith, Byron B., Ph.B. (Columbia), 19, East 74th-street, New York City, U.S.A.
1898		Goldsmith, John Naish, B.Sc. (Vict.), Ph.D. (Heidelberg), 67, Chancery-lane, W.C.
1897		Gomess, Alfred Francis Bilderbeck, M.R.C.S. (Eng.), L.R.C.P. (Lond.), 33, Drayton-gardens, South Kensington, S.W.
1911		Gonville, Cyril Herbert Koszelski, 63, The Broadway, Stratford, E.
1904		‖Goodson, John Augustus, F.I.C., 101, East-street, Epsom
1904	Trans.	Goodwin, Leo Frank, Ph.D. (Heidelberg), A.C.G.I., F.I.C., Queen's University, Kingston, Ontario, Canada
1896	Trans.	Goodwin, William, M.Sc. (Manc.), Ph.D. (Göttingen), The Midland Agricultural and Dairy College, Kingston, Derby

Date of Election.			
1911			Goold, Rowland Lewis, F.C.I.P.A., Assoc.I.E.E., 5, Corporation-street, Birmingham.
1875			Gordon, Joseph Gordon, F.I.C., Queen Anne's-mansions, Westminster, S.W.
1905			Gorman, Henry Isaac, 126, Quay, Waterford, Ireland
1909	Trans.		Gortner, Ross Aiken, Associate Professor, M.A. (Toronto), B.Sc. (Nebraska), Ph.D. (Columbia), The University of Minnesota, University Farm, St. Paul, Minnesota, U.S.A.
1890			Gossling, Frank, B.Sc. (Lond.), H.M. Patent Office, Staple Inn, W.C.
1916			Goto, Kakuji, Chemical Laboratory, University College, Gower-street, W.C.
1889	Trans.		‖Gott, Benjamin Scaife, M.A. (Cantab.), Middlesex Education Committee, Queen Anne's-chambers, 28, Broadway, Westminster, S.W.
1897	Trans.		‖Goulding, Ernest, D.Sc. (Lond.), F.I.C., 88, Sylvan-avenue, Chitts Hill, N.
1887			Gover, Herbert James, 29, Piccadilly, Hanley, Staffs.
1889			Gow, Robert John, Ivy Lea, Hough Green, Widnes
1893			Gower, Alfred Roland, Ashleigh, Furness-park-road, Barrow
1871	Trans.	(C. 1898-) (01, 1906-7)	‖Gowland, William, Prof., A.R.S.M., F.R.S., F.I.C., 13, Russell-road, Kensington, W.
1916			Grace, Claude Saville, B.Sc., F.I.C., 36, Harvard-road, Gunnersbury, W.
1915			Graham, Charles Stanley, 174, Frodingham-road, Scunthorpe, Lincs.
1880	Trans.		‖Graham, Christopher Colborne, F.I.C., Oriel House, Scarborough
1910			Gramont, Count Arnaud de, D. ès Sc., Membre de l'Institut de France, 179, Rue de l'Université, Paris, France
1890	Trans.		Grant, James, M.Sc. (Manc.), F.I.C., Oaklands, Gardner-road, Prestwich, Manchester
1887			Gravill, Edward Day, 42, Walmsley-street, Hull
1882			‖Gray, George, Lyndhurst, Lincoln, New Zealand
1913			Gray, George Watson, F.I.C., 8, Inner Temple, Liverpool
1912			Gray, Harold Heath, B.Sc. (Manc.), 12, Sach-road, Upper Clapton, N.E.
1900	Trans.		Gray, Robert Whytlaw, Ph.D. (Bonn), Eton College, Windsor
1892	Trans.		‖Gray, Thomas, Prof., D.Sc. (Glas.), Ph.D. (Jena), The Royal Technical College, Glasgow
1895			Greaves, William Abraham, B.Sc. (Lond.), 23A, Broad-bank, Louth

Date of Election.			
1885	Trans.	C. 1894-5	‖Green, Arthur George, Prof., Hon. M.Sc. (Vict.), F.R.S., F.I.C., 49, Cardigan-road, Headingley, Leeds
1902	Trans.		Green, Clarence James, B.Sc. (Vict.), c/o Messrs. Nicholson and Co., Beaumont Works, St. Albans
1905			Green, Ernest, 98, Cheadle-road, Cheadle Hulme, Stockport
1908			Green, Henry Hamilton, B.Sc. (Glas.), Laboratories for Veterinary Research, Department of Agriculture, Onderstepoort, Pretoria, S. Africa
1878			Green, Herbert, Hayle Mill, Maidstone
1887			Green, John Edward, A.R.S.M., F.I.C., West Clyne, Stretford, Manchester
1878			Green, Lawrence, Lower Tovil, Maidstone
1916			Green, Samuel Harold, St. Neots Villa, Lelant, Cornwall
1907	Proc.		Green, William Heber, D.Sc. (Melbourne), The University, Melbourne, Australia
1874	Trans.		‖Greenaway, Alfred John, F.I.C., The Orchard, Chertsey, Surrey
1907			Greenough, Thomas Rigby, B.A. (Cantab.), F.I.C., Beechwood, Leigh
1885			Greenway, Thomas John, F.I.C., 369, Collins-street, Melbourne, Australia
1916	Trans.		Greenwood, Harold Cecil, D.Sc. (Manc.), 10, University Mansions, Putney, S.W.
1894	Proc.		‖Greeves, Alfred, B.Sc. (Lond.), A.R.C.S., F.I.C., Wandsworth Technical Institute, Wandsworth, S.W.
1891			Gregory, Alfred John, M.D. and B.S. (Dun.), M.D. (Cape of Good Hope), M.R.C.S. and D.P.H. (Eng.), c/o The National Bank of S. Africa, 117, Cannon-street, E.C.
1906	Trans.		Gregory, Thomas William Diggle, Kinross, Trentham, Stoke-on-Trent
1896			Grice, Walter Thomas, c/o A. Symington, Esq., Allanton, Auldgirth, Dumfries
1910			Grieve, James, 43, Cedars-road, Beckenham
1908			Griffin, John, B.A. (Cantab.), 9, Firs-avenue, Muswell Hill, N.
1888			‖Griffith, David Agnew, Silver Leigh, Poll Hill-road, Heswall, Heswall Hill, Birkenhead
1911			Griffiths, Evan Dalton, B.Sc. (Wales), 9, Wanstead Park-avenue, Manor Park, E.
1905			Griffiths, John, B.Sc. (Wales), 7, Thorndale-avenue, Larne, Ireland
1902			Griffiths, John Thomas, B.Sc. (Lond.), Green-hill, Tenby, S. Wales
1902			Grimwade, Wilfrid Russell, B.Sc. (Melbourne), 342–346, Little Flinders-street, Melbourne, Australia

Date of Election.			
1893			Grimwood, Robert George, F.I.C., 43, Leaside-avenue, Muswell Hill, N.
1906			Grindley, Harry Sands, Prof., D.Sc. (Harvard), B.Sc. (Illinois), State University, Urbana, Ill., U.S.A.
1914			Grinling, George Noel, A.I.C., 61, Cartwright-gardens, W.C.
1889			Gripper, Harold, Great Central Railway, Gorton, Manchester
1909			Grist, Charles James, Elgin House, Knockholt, Sevenoaks
1900			Gritton, Henry Bertie, The Royal Mint, Sydney, N.S.W.
1895			Grossmann, Edward Henry, 8, Onslow-place, South Kensington, S.W.
1871	Trans.	C. 1877-8; 1909-12; V.P. 1899-02	‖Groves, Charles Edward, F.R.S., F.I.C., Kennington Green, S.E.
1905			Groves, Samuel Ernest, 3, Ripon-gardens, Jesmond, Newcastle-on-Tyne
1906			Grubb, David Paton, B.Sc. and B.Sc.Eng. (Edin.), A.R.S.M., 39, Victoria-road, Barnsley
1897			Grundey, Frederick Roscoe, B.Sc. (Vict.), Edale, Albany-road, Douglas, Isle of Man
1912			Grützmacher, Frederick Lyle, Church of England Grammar School, North Sydney, N.S.W.
1910			Guhlmann, Charles Frederick, c/o The Grasselli Chemical Co., Arcade Building, Cleveland, Ohio, U.S.A.
1902			Gumersall, Edward, 61, Bartholomew-road, N.W.
1895			Gunn, Alexander, 5, Leppoe-road, Clapham Park, S.W.
1906			Gupta, Hem Chandra Dutt, Prof., M.A. (Calcutta), Gupta-Nibas, Krishnagar, Dist. Nadia, Bengal, India
1904	Trans.		Guthrie, John Monteath, 199, Ferry-road, Leith
1902	Trans.		Haas, Paul, D.Sc. (Lond.), Ph.D. (Freiburg), 11, Westbourne-park-road, W.
1910	Trans.		Hackford, John Edward, B.Sc. (Lond.), F.I.C., c/o Messrs. S. Pearson and Son, 47, Parliament-street, Westminster, S.W.
1894			Hadley, Arthur, c/o Messrs. Georges Brewery, Ltd., Bristol
1893			‖Hadley, Henry Edwin, B.Sc. (Lond.), A.R.C.S., School of Science, Kidderminster
1881			Hailes, Alfred James de, F.I.C., 15, Red Lion-square, W.C.
1892			Haines, Walter Stanley, Prof., c/o Rush Medical College, Chicago, Ill., U.S.A.
1876	Trans.		Hake, Henry Wilson, Ph.D. (Giessen), F.I.C., Westminster Hospital Medical School, Caxton-street, S.W.
1912			Hale, Arthur James, B.Sc. (Lond.), F.I.C., 74, Taybridge-road, Lavender Hill, S.W.

Date of Election.			
1893			Hale, Henry Ormsby, M.A. (Cantab.), Oundle School, Oundle
1914			Hale, James Stanley, Principe 4, Bilbao, Spain
1891	Trans.	C. 1904–7	Hall, Alfred Daniel, M.A. (Oxon.), F.R.S., Ewhurst, Mostyn-road, Merton, S.W.
1889			Hall, Allan Twistleton, c/o Messrs. Sissons Bros. and Co., Ltd., Hull
1911			Hall, Arthur Bennett, c/o Messrs. Boots, Ltd., 13, Market-street, Wellingborough
1889	Trans.		Hall, John Albert, Lieut.-Col., M.Sc. (Manc.), Longstone, Esquimault-road, Victoria, British Columbia
1903			Hall, John Thomas, West View, Stanwell, Staines
1899			‖Hall, Samuel Godfrey, c/o Messrs. Edward Cook & Co., Works, Bow, E.
1911			Hall, Sydney, B.Sc. (Manc.), The Grammar School, Alcester, Warwickshire
1886			Halliburton, William Dobinson, Prof., M.D., B.Sc. and F.R.C.P. (Lond.), M.R.C.S. (Eng.), F.R.S., King's College, Strand, W.C.
1897			Halliwell, Edward, F.I.C., c/o Ribble Joint Committee, 2, Stanley place, Preston
1900			Halstead, Reginald Gordon, 12 and 16, Coleman-street, E.C.
1906			‖Hamer, John, 158, Darwen-road, Bromley Cross, Bolton
1888	Trans.		Hamilton, James Cullen, Barrows-green, near Kendal
1898			Hamilton, Oswald, Old Stratford, Stony Stratford, Bucks.
1904			Hammond, Harold Sankey, Macdonald College, St. Anne de Bellevue, Quebec, Canada
1901			Hammond, Herbert Blackmore, 101, Barton-road, Dover
1911	Trans.		Hampshire, Charles Herbert, B.Sc. (Lond.), F.I.C., University College Hospital, Gower-street, W.C.
1900			Handcock, Walter Augustus, F.I.C., 5, Dryburgh-mansions, Putney, S.W.
1895	Trans.		Hanes, Edgar Septimus, F.I.C., 34, Sarre-road, West Hampstead, N.W.
1910			Hanley, John, F.I.C., 7, University-road, Bootle, Liverpool
1889			‖Hanson, Alfred Miall, The Marjorie, Whalley, Blackburn
1901	Trans.		Hanson, Edward Kenneth, M.A. (Cantab.), F.I.C., Woodthorpe, Royston-park-road, Hatch End, Middlesex; and 2A, The Parade, High-street, Watford
1906			Hanson, Harold Norman, Field Head, Brighouse
1895			Hanson, Weldon, Westwick, Ashville-avenue, Norton, Stockton-on-Tees
1897			Harbord, Frank William, A.R.S.M., F.I.C., Surbiton House, Englefield Green, Surrey

Date of Election.			
1859	Trans.	S. 1865-73; V. P. 73-6, 80-3, 92-5; P. 1895-7	‖Harcourt, Augustus George Vernon, M.A. and Hon. D.Sc. (Oxon.), Hon. D.C.L. (Dun.), Hon. LL.D. (Montreal), F.R.S., F.I.C., St. Clare, Ryde, Isle of Wight
1887	Trans.	C. 1902-05, 1912-15	‖Harden, Arthur, Prof. D.Sc. (Vict.), Ph.D. (Erlangen), F.R.S., F.I.C., 5, Cambridge-gardens, Marlborough-road, Richmond, Surrey
1911			Harding, Henry George Alan, Darling-street, Chatswood, Sydney, N.S.W.
1912			Harding, Leonard, Rivoli, Portland-road, Ellesmere-park, Eccles
1909	Trans.		Harding, Victor John, D.Sc. (Manc.), A.I.C., McGill University, Montreal, Canada
1909			Hargreaves, Egerton, M.Sc. (Manc.), Corris, Belgrave-crescent, Woods Moor, Stockport
1884			Hargreaves, John, F.I.C., Widnes
1913			Hargreaves, Richard, B.A. (Cantab.), Inglewood, Penrith
1900			Hargreaves, William Arthur, M.A. and B.C.E. (Melbourne), F.I.C., Globe-chambers, Victoria-square-west, Adelaide, S. Australia
1900			‖Harker, George, D.Sc. (Lond.), Chemical Dept., The University, Sydney, N.S.W.
1878			‖Harland, William Dugdale, 48, King-street, Manchester
1897			‖Harley, Vaughan Berkeley, Prof., M.D. (Edin.), M.R.C.P. (Lond.), 25, Harley-street, W.
1897			Harman, Harold Wallis, 24, Holborn-viaduct, E.C.
1903			Harmer, Francis Gerald, Cockburn High School, Leeds
1899			Harper, Henry Winston, M.D. (Virginia), The University of Texas, and 2216, Rio Grande-street, Austin, Texas, U.S.A.
1914			Harper, Theophilus, 39, Camden-street, University-road, Belfast
1914			Harrap, Eric Russell, The Laurels, Netherby-road, Forest Hill, S.E.
1916			Harrap, Frank Nettleton, M.Sc. (Leeds), 116, Dumbreck-road, Eltham, S.E.
1907			Harrington, Arthur George, F.I.C., Municipal Buildings, Singapore, Straits Settlements
1881			Harrington, William Bury, Leeview, Montenotte, Cork
1896			Harris, Frederick William, F.I.C., Tontine Buildings, 20, Trongate, Glasgow
1893			Harris, Harold, The Birmingham Metals and Munitions Co., Ltd., Ammunition Factory, Streetly, Birmingham
1895			Harris, Harry, A.R.S.M., c/o Messrs. H. J. Enthoven & Sons, Ltd., Upper Ordnance Wharf, Rotherhithe, S.E.
1878			‖Harris, Thomas Frederick, B.Sc. (Lond.), Springfield, Hythe
1914			Harrison, Alfred Cornwell, Box 47, Penhalonga, Rhodesia, S. Africa

Date of Election.		
1894	Trans.	Harrison, Edward Frank, Major, B.Sc. (Lond.), F.I.C., 57, Chancery-lane, W.C.; and Langholm, Edgar-road, S. Croydon
1888		Harrison, John Burchmore, C.M.G., M.A. (Cantab.), F.I.C., Government Laboratory, Georgetown, Demerara, British Guiana
1902		Harrison, Walter Ernest, 17, Soho-road, Handsworth, Birmingham
1901		Harry, Frederick Thomas, 92, Rodenhurst-road, Clapham Park, S.W.
1886		Hart, Bertram Harvey, Rosslyn, High-street, Sidcup, Kent
1900		Hart, Herbert William, Garth, Clifton Drive, Lytham
1891		Hart, William Beamont, F.I.C., Laboratory, 8, Exchange-street, Manchester
1882		Hartley, Arthur, The Brewery, Emsworth, Hants.
1897	Trans.	Hartley, Ernald George Justinian, B.A. (Oxon.), The Bungalow, Foxcombe Hill, near Oxford
1912	Trans.	Hartley, Harold, M.Sc. (Manc.), c/o The Richmond Gas Stove and Meter Co., Ltd., Academy-street, Warrington
1899	Trans.	Hartley, Harold Brewer, M.A. (Oxon.), Balliol College, Oxford
1890	Trans.	Hartog, Philip Joseph, M.A. (Manc.), B.Sc. (Lond. and Vict.), University of London, South Kensington, S.W.
1900	Trans.	‖Hart-Smith, James, A.R.C.S., F.I.C., The Secondary School, Latchmere-road, Battersea, S.W.
1900	Trans.	‖Harvey, Alfred William, 136, Bargery-road, Catford, S.E.
1909		Harvey, Arthur John, 18, Shoebury-road, East Ham, E.
1885		Harvey, Ernest William, A.R.S.M., 36, Arthur-road, Wimbledon Park, S.W.
1907		Harvey, Thomas Featherstone, 5, Park Hill-road, Chingford, N.E.
1911		Harwood, Henry Francis, M.Sc. (Manc.), Ph.D. (Heidelberg), Pendeen, Station Gates, Beaconsfield, Bucks.
1914		Haskew, Richard Selwyn, A.C.G.I., 103, Hampton-road, Forest Gate, E.
1894		Hatfield, John Adams, F.I.C., c/o Messrs. J. Lysaght, Ltd., Orb Iron Works, Newport, Mon.
1912		‖Hatherly, Henry Medley, 14, Stackpool-road, Southville, Bristol
1892		Hatton, William Percy, c/o Messrs. W. R. Hatton and Sons, Ltd., Fells Haugh, Horn-lane, Acton, W.
1880		Hawkes, Alfred Edward, M.D. (Brussels), L.R.C.P. (Edin.), Muspratt Laboratory, The University, Liverpool
1916	Trans.	Hawkins, Ernest Mostyn, F.I.C., South Eastern Laboratory, Watling Chambers, Canterbury
1894	Trans.	Haworth, Edward, D.Sc. (Vict.), Beaconhurst, Weston-road, Runcorn
1898		Haworth, John, 117, Millhouses-lane, Sheffield

Date of Election			
1909	Trans.		Haworth, Walter Norman, D.Sc. (Manc.), Ph.D. (Göttingen), United College, The University, St. Andrews
1913			Hay, Alexander Houghton, Essex Wharf, Narrow-street Limehouse, E.
1907			Hay, William, c/o Messrs. William Hay, Ltd., 42–46, Walmsley-street, Hull
1910			Haycock, John, Hill Top House, Great Glen, Leicester
1912			Haydon, Archie, 55, Grove-lane, Kingston-on-Thames
1910	Trans.		Hayhurst, Walter, M.Sc. (Manc.), Hameldon, Manchester-road, Accrington
1900			‖Haynes, James Herbert, B.Sc. (Vict.), Sennen, 65, Kennington-avenue, Ashley Down, Bristol
1909			Hayward, Eric, F.I.C., c/o W. R. Criper, Esq., Konnagar House, Konnagar, Calcutta, India
1906			Hayworth, William Prince, F.I.C., 24, Tower-road, Dartford
1915			Heap, Harri, M.Sc. (Manc.), F.I.C., Brunside, Lyndhurst-road, Withington, Manchester
1903			Heasman, Harold Montague, 26, Tothill-street, S.W.
1891			Heath, John William, Royal Institution, Albemarle-street, W.
1898			Heaton, John, Southcliffe, Roker, Sunderland
1902			Heaton, Noël, B.Sc. (Lond.), 72, Abbey-road, N.W.
1913			Hebden, George Alfred, 3, Park-terrace, Thrybergh, Rotherham
1906	Trans.		Hedley, Edgar Percy, Ph.D. (Leipzig), A.R.C.S.I., 38, Bessborough-road, Birkenhead
1899			Hedley, George Ward, M.A. (Oxon.), The College, Cheltenham
1905			Heely, Frederick William, Analytical Laboratory, West-street, Alford, Lincs.
1876		C. 1895-9	Hehner, Otto, F.I.C., 11, Billiter-square, E.C.
1912	Trans.		Heilbron, Isidor Morris, Ph.D. (Leipzig), F.I.C., 7, Claremont-terrace, Glasgow
1889			Helbing, Heinrich B., 81, Queen Victoria-street, E.C.
1875			‖Hellon, Robert, Ph.D. (Heidelberg), A.R.S.M., F.I.C., Whinthwaite, Seascale, viâ Carnforth
1872			‖Helm, Henry James, I.S.O., F.I.C., Simonstone, 27, Hammelton-road, Bromley, Kent
1899			Hembrough, James, A.R.C.S., A.I.C., Science, Art and Technical School, Market-street, Newton Abbot
1900			Hemingway, Frank Christian Richard, 6, East Union-avenue, Bound Brook, N.J., U.S.A.
1915			Henchley, Albert Richard, Major, R.A.M.C., M.D. (Brussels), L.R.C.S., L.R.C.P., and L.M. (Edin.), L.F.P.S. (Glasgow), L.S.A. (Lond.), 91, Siddals-road, Derby
1914			Henderson, Frederick George, 44, Dene-view, Wallsend-on-Tyne

Date of Election.			
1885	Trans.	V.P. 1916-	‖Henderson, George Gerald, Prof., M.A., D.Sc. (Glas.), Hon. LL.D. (St. Andrews) F.R.S., F.I.C., The Royal Technical College, 204, George-street, Glasgow
1895	Trans.		Henderson, James, Ph.D. (München), B.Sc. (St. Andrews), c/o Horlick's Malted Milk Co., Racine, Wisconsin, U.S.A.
1905	Trans.		Henderson, James Alexander Russell, D.Sc. (Glas.), 21, Islam-road, Sale, Manchester
1900	Trans.		Henderson, John Brownlie, F.I.C., Government Analyst, Brisbane, Queensland
1916			Henderson, Thomas Bertram, 44, Dene View, Wallsend-on-Tyne
1892			Hendrick, James, Prof., B.Sc. (Lond.), F.I.C., Marischal College, Aberdeen
1903			Hendrickson, Arthur V., The Gas Works, Lower Sydenham, S.E.
1909			Hendry, Robert Douglas, 16, Church-street, Alloa
1912			Henius, Max, Ph.D. (Marburg), 1135, Fullerton Avenue, Chicago, Ill., U.S.A.
1901			‖Henley, The Hon. Francis Robert, M.A. (Oxon.), F.I.C., 49, Montagu-square, W.
1905			Hennings, Carl Richard, Ph.D. (Freiburg), 19, St. Dunstan's-hill, E.C.
1914			Henri, Victor, Prof., 106, Rue Denfert-Rocherau (XIV.), Paris
1899	Trans.		‖Henry, Thomas Anderson, D.Sc. (Lond.), Scientific and Technical Department, Imperial Institute, S. Kensington, S.W.
1905	Trans.		Henstock, Herbert, M.Sc. (Vict.), Ph.D. (Zürich), Wilcott House, Wilcott, near Nesscliffe, Shrewsbury
1913			Henville, Douglas, F.I.C., 40, Lowgate, Hull
1904			Henzell, Archie Willoughby, Rev., c/o Rev. Dr. T. J. Bensley, P.O. Box 58, Palmyra, New Jersey, U.S.A.
1871	Trans.		Herman, Douglas, F.I.C., Rainhill, Lancs.
1912			Heron, Harold, 110, Fenchurch-street, E.C.
1908			Heron, John Maxwell, Stapenhill, High-street, Mistley, Manningtree, Essex
1906			Herty, Charles Holmes, Prof., Ph.D. (Johns Hopkins), Ph.B. (Georgia), University of North Carolina, Chapel Hill, N.C., U.S.A.
1913			Hewitt, James Arthur, B.Sc. (St. Andrews), 100, Rothwell-street, Glasgow
1892	Trans.	C. 1903-05, 1908-11	‖Hewitt, John Theodore, Major, M.A. (Cantab.), D.Sc. (Lond.), Ph.D. (Heidelberg), F.R.S., Clifford House, Staines-road, Bedfont, Feltham, Middlesex
1900			Hewitt, Samuel, 53, Dover-street, Unthank-road, Norwich
1892			Hewlett, John Cooke, 35–42, Charlotte-street, Great Eastern-street, E.C.
1883	Trans.	C. 1897-1901, V.-P. 1914-	‖Heycock, Charles Thomas, M.A. (Cantab.), F.R.S., 3, St. Peter's-terrace, Cambridge

Date of Election.			
1876	Trans.		Hibbert, Walter, F.I.C., 60, Prebend-gardens, Stamford Brook, Hammersmith, W.
1881			‖Hiddingh, Michael, Newlands, near Capetown, S. Africa
1905			Higgins, John Michael, 39, Queen-street, Melbourne, Australia
1907			Higham, Richard, 161, Mauldeth-road, Withington, Manchester
1909			Higson, Frank, Lymehurst, Victoria-avenue, Cheadle Hulme, Stockport
1908	Trans.		Hilditch, Thomas Percy, D.Sc. (Lond.), F.I.C., Birchdene, Cross-lane, Grappenhall, Cheshire
1896	Trans.		Hill, Arthur Croft, M.A., M.D. and B.S. (Cantab.), M.R.C.S. (Eng.), L.R.C.P. (Lond.), 169, Cromwell-road, S.W.
1896		C. 1916-	‖Hill, Charles Alexander, B.Sc. (Lond.), F.I.C., 26, Courtfield-gardens, S.W.
1896	Trans.		Hill, Ernest George, Prof., Sc.D. (Dub.), B.A. and B.Sc. (Oxon.), Muir College, Allahabad, India
1912			Hill, James Grainger, 421, Stourbridge-road, Holly Hall, Dudley
1911			Hill, James Hogan, c/o Opium Dept., Fyzabad, U.P., India
1913			Hill, Percy Wolmer, Highbury, Vicarage-road, Wednesbury
1905			Hill, William Basil, Eastfield, Stockton-lane, York
1894			‖Hills, Edmond Herbert, Capt. R.E., F.R.S., 32, Prince's-gardens, S.W.
1892			‖Hills, Harold Fletcher, Commercial Gas Works, Stepney, E.
1906			Hills, James Stuart, F.I.C., Oxford Works, Tower Bridge-road, S.E.
1873			‖Hills, Walter, 50, Wigmore-street, W.
1896			Hinchley, John William, A.R.S.M., 55, Redcliffe-road, S.W.
1915			Hinde, Charles, 6695, Culloden-avenue, South Vancouver, B.C., Canada
1914			Hinkel, Leonard Eric, B.Sc. (Lond.), F.I.C., Bucklands, Old Oak-road, Acton, W.
1908			Hinks, Edward, B.Sc. (Lond.), F.I.C., 16, Southwark-street, S.E.
1900			Hinks, Percy John, A.R.C.S., F.I.C., Woodstock, Beaconsfield-road, Blackheath, S.E.
1870			Hislop, George Robertson, Gasworks, Blackstoun-road, Paisley
1898			‖Hislop, Lawrence, Gasworks, Uddingston, Glasgow
1898			Hislop, Robert Findlay, Greenhill House, Paisley
1883			‖Hobbs, Bedo, Lamb Brewery, Chiswick, W.
1905			Hobsbaum, Isaac Berkwood, 13, Paget-road, Stoke Newington, N.
1914			Hobson, Arthur Bertram, M.Sc. (Manc.), 6, West View, Highgate Hill, N.
1901			Hobson, Edwin, Howdendyke, Howden, Yorks.
1884			Hodges, Herbert John, Brewery House, York-building Southampton
1913			Hodges, Richard Pendarves, 42, Olive-road, Cricklewood, N.W.

Date of Election.			
1914			Hodges, Trevor Edward, 43, Stapleton Hall-road, Stroud Green, N.
1882	Trans.		‖Hodgkin, John, F.I.C., 131, Hamlet-gardens-mansions, Ravenscourt Park, W.
1879	Trans.	C. 1883-5, 1907-10	Hodgkinson, William Richard Eaton, Prof., Ph.D. (Würzburg), F.I.C., 89, Shooter's Hill-road, Blackheath, S.E.
1911			Hodgson, Cyril Vincent, 181, Watlands-view, Wolstanton, Stoke-on-Trent.
1873			‖Hodgson, Henry Tylston, M.A. (Cantab.), Harpenden, Herts.
1904			Hodgson, Thomas Reginald, M.A. (Cantab.), F.I.C., 34, John Dalton-street, Manchester
1911	Trans.		Hodsman, Henry James, M.Sc. (Leeds), Dept. of Fuel and Coal Gas Industries, The University, Leeds
1913			Hodsoll, Harold Edward Pollock, c/o Messrs. Renny, Forbes & Co., Ltd., Alperton, Wembley, Middlesex
1911			Hogg, Alexander Frederick, M.A. (Cantab.), 61, Hervey-road, Blackheath, S.E.
1876			Holcroft, Harold, M.A. (Cantab.), Parkdale, Wolverhampton
1912			Holden, Edmund Haworth, M.Sc. (Vict.), Springhill, Higher Cloughfold, Manchester
1908			Holland, Frank William Crossley-, 55, Glasslyn-road, Crouch End, N.
1908			Holland, Norman, 606, Grosvenor-avenue, Westmount, Montreal, Canada
1913	Trans.		Hollely, William Francis, A.I.C., 67, Ross-road, Wallington, Surrey
1902			Hollingworth, David Vincent, Birchenwood Collieries, Kidsgrove, Stoke-on-Trent
1905			Hollins, Cecil, B.Sc. (Lond.), c/o Mrs. Blake, Craig-y-don, Hawarden, Chester
1886			Holloway, George Thomas, A.R.C.S., F.I.C., 9-13, Emmett-street, Limehouse, E.
1895			Holme, Arthur Edward, M.A. (Oxon.), The Wheelwright Grammar School, Dewsbury
1897	Trans.		Holmes, John, Government Laboratory, Clement's Inn Passage, W.C.
1898	Trans.		Holroyd, George William Fraser, M.A. (Oxon.), The Chemical Works, Shoreham, Sussex
1913			Holroyd, Thomas Arthur, B.Sc. (Leeds), Carnbuck Club, Perambore Barracks, Madras, India
1902	Trans.		‖Holt, Alfred, M.A. (Cantab.), D.Sc. (Manc.), Dowsefield, Allerton, Liverpool
1914			Holt, Alfred, 32, Britain-street, Bury
1910			Holt, Fred., M.Sc. (Manc.), 28, Mere-street, Rochdale

Date of Election			
1913			Holt, William Joseph, 31, Spruce Hills-road, Walthamstow, N.E.
1893			Holthouse, Harold Bertram, 106, Radcliffe-road, West Bridgford, Nottingham
1898			‖Homfray, David, B.Sc. (Lond.), F.I.C., c/o Senores La Compania de Fabricas de Papel de San Rafael, Apartado No. 469, Mexico City
1878			Hooker, Ayerst Henham, F.I.C., Board of Health, Cairo, Egypt
1892	Trans.		Hooker, Samuel Cox, Ph.D. (Munich), 82, Remsen-street, Brooklyn, N.Y., U.S.A.
1883			‖Hooper, David, Hon. LL.D. (McMaster Univ., Toronto), F.I.C., East Riggs, Dornock, Annan
1888		C. 1907-08	‖Hooper, Egbert Grant, F.I.C., 16, Royal-avenue, Sloane-square, S.W.
1891			‖Hooper, Ernest Frederick, 10, Elms-west, Sunderland
1912	Trans.		Hope, Edward, D.Sc. (Manc.), University Chemical Laboratories, The Museum, Oxford
1907			Hope, Geoffrey Dodleston, B.Sc. (Vict. and L'pool.), Ph.D. (Halle), c/o Indian Tea Association, Calcutta, India
1906			Hopkins, Frederick Gowland, Prof., M.A. (Cantab.), M.B., D.Sc., and L.R.C.P. (Lond.), M.R.C.S. (Eng.), F.R.S., F.I.C., Saxmeadham, Grange-road, Cambridge
1909			Hopkinson, Reginald, B.Sc. (Lond.), Cromwell Lodge, Huntingdon
1904			Horn, George Mathieson, Capt., The Laboratory, Clarnico Confectionery Works, Victoria Park, N.E.
1908			Hornby, Percy Hulme, c/o The Brentford Gas Co., Southall
1894			‖Hornby, Richard, M.A. (Oxon.), Haileybury College, Hertford
1911			Horne, William Joseph Chetwynd, c/o Messrs. Cleeve Bros., Lansdowne, Limerick; and Walnut House, Limerick, Ireland
1908			Horrobin, Arthur, c/o Bombay, Baroda and Central India Railway Co., Ajmer, Rajputana, India
1904			Horrod, George William Thomas, c/o Messrs. Fassett & Johnson, 86, Clerkenwell-road, E.C.
1897			Horseman, James Walter, Wellington College, Wellington College Station, Berks.
1892			Horsfall, John, 4, Grange-avenue, Rawtenstall, Manchester
1901	Proc.		Horton, Edward, B.Sc. (Lond.), Lawes Agricultural Trust, Rothamsted Experimental Station, Harpenden, Herts.
1909			Hoseason, James Henry, Stanley Bank, Chesham-place, Bowdon, Altrincham
1902			Hosking, Arthur Francis, c/o The Tasmania Gold Mining Co., Ltd., Beaconsfield, Tasmania
1886			‖Hoskins, Arthur Percy, F.I.C., Clonlee, Rosetta-park, Belfast
1911			Hough, Bernard Grindrod, The Chestnuts, Wardle-road, Sale, Manchester

Date of Election.			
1909			Hough, Ralph, Newlands, Wilbraham-road, Alexandra-park, Manchester
1887	Proc.		Houlding, William, B.Sc. (Edin.), 34, Tynemouth-street, Liverpool
1882			‖Howard, Alfred Gravely, Burnt House, Chigwell, Essex
1870		C. 1875-9, 83-5, 98-1902. V.P. 1886-9, 1903-06	‖Howard, David, J.P., F.I.C., Devon House, Buckhurst Hill, Essex
1887	Trans.		‖Howard, David Lloyd, c/o Messrs. Howards & Sons, Ltd., Uphall Works, Ilford, E.
1889			Howard, George William, Calverley, Tunbridge Wells
1875			Howard, Thomas, F.I.C., 50, Ellington-street, Liverpool-road, N.
1903			Howarth, John George, Danes Dyke, Reigate-road, Reigate, Surrey
1882			Howe, James Lewis, Prof., M.D. (Louisville), Ph.D. (Göttingen), B.A. (Amherst), Washington and Lee University, Lexington, Va., U.S.A.
1913			Howells, Alfred Leslie, B.Sc. (Lond.), Bath Villa, Lydney
1912			Howells, Oliver Richard, B.Sc. (Lond.), County Secondary School, Stowmarket
1905			Howgate, James Henry, B.A. (Lond.), The Grammar School, Huntingdon
1876			Howie, William Lamond, 26, Neville-court, Abbey-road, N.W.
1903			Howorth, Franklin Wise, 10, New-court, Lincoln's Inn, W.C.
1915			Hoy, Ernest James, 474, Park-road-north, Claughton, Birkenhead
1889			‖Hoyle, Richard Ashworth, Elm-grove, Fairlawn-road, Lytham, Lancs.
1889			‖Hoyles, Henry Richardson, 10, Fore-street, Wellington, Somerset
1907			‖Hubbard, The Hon. Raymond Egerton, B.A. (Oxon.), c/o Messrs. Egerton, Hubbard & Co., Petrograd, Russia; and Addington Manor, Winslow, Bucks.
1910			Huck, John, M.A. (Cantab.), 15, Clifton-road, Crouch End, N.
1914			Hudleston, Lawson John, B.Sc. (Lond.), 68, Parliament Hill, Hampstead, N.W.
1899	Trans.		Hübner, Julius, M.Sc. (Manc.), F.I.C., The Municipal School of Technology, Manchester
1916			Huggins, Albert Francis, Cartref, Cromford-road, West Bridgford, Nottingham
1911			Hughes, Edwin Burnhope, B.Sc. (Lond.), Royal College, Mauritius
1903			Hughes, Edwin Reginald, 106, Queen Victoria-street, E.C.
1907			Hughes, Francis Townshend Cunynghame, Lieut.-Col., H.M.'s Assay Office, 47/1, Strand-road, Calcutta, India
1894	Trans.		‖Hughes, Frank, Turf Club, Cairo, Egypt
1880	Trans.		Hughes, George Henry, 155, Fenchurch-street, E.C.

Date of Election.		
1910		Hughes, Herbert Hillier, B.Sc. (Lond.), The Grammar School, Tottenham, N.
1868		Hughes, John, F.I.C., Analytical Laboratory, 79, Mark-lane, E.C.
1912		Hughes, John Owen, B.Sc., University College of N. Wales, Bangor
1908		Hughes, Joseph Albert, School of Mines, Charters Towers, Queensland, Australia
1896		‖Hughes, Joshua Arthur, The Square, Abercarn, Mon.
1885		Hughes, Theophilus Vaughan, A.R.S.M., F.I.C., Admont, Coed Coch-road, Old Colwyn, Colwyn Bay
1882		Hughes, Thomas, F.I.C., Borough Analyst's Office, 31, Loudoun-square, Cardiff
1908	Trans.	Hull, Thomas Ernest, Woodlands View, Newland-avenue, Birkby, Huddersfield
1904		Hulme, John, Ph.D. (Halle), Roselands, Hurdsfield, Macclesfield
1907	Trans.	Humphries, Herbert Brooke Perren, B.Sc. (Lond.), A.R.C.S., Queen Anne's-chambers, Westminster, S.W.
1883		Humphrys, Norton Henry, 5, Wyndham-road, Salisbury
1885		Hunter, Matthew, M.A. (Oxon.), Rangoon College, Rangoon, Burma
1893	Trans.	Huntly, George Nevill, B.Sc. (Lond.), A.R.C.S., F.I.C., 14, Old Queen-street, Westminster, S.W.
1914		Hurford, Thomas Clifton, c/o The Tongkah Harbour Tin Dredging Co., Puket, W. Siam
1911		Hurst, Reginald, 233, Bellingham-road, Catford, S.E.
1902	Trans.	Hurtley, William Holdsworth, D.Sc. (Lond.), St. Bartholomew's Hospital, E.C.
1861		Huskisson, Henry Owen, F.I.C., Moon-street, Theberton-street, Islington, N.
1900		Hutchin, Henry William, Lamorna, Trelawny-road, Camborne, Cornwall
1894		Hutchinson, Alfred, M.A. (Cantab.), B.Sc. (Lond.), 3, Windsor-road, Saltburn-by-the-Sea
1890	Trans.	‖Hutchinson, Arthur, M.A. (Cantab.), Ph.D. (Würzburg), Pembroke College, Cambridge
1908		Hutchinson, Henry Brougham, Ph.D. (Göttingen), Wyver, Spenser-road, Harpenden, Herts.
1913		Hutchinson, James Joseph, The Biscuit Factory, Bishop-street, Dublin
1913		Hutchinson, Percy, B.Sc. (Lond.), Aden House, Manchester-road, Bury
1907		‖Hutchinson, William Doge, B.A. (Oxon.), Ungeverstrasse 11 (I), Munich, Germany
1913		Huxtable, Charles, Devonia, Menlove-avenue, Liverpool

Date of Election		
1913	Trans.	Hynd, Alexander, M.A., D.Sc. (St. Andrews), School of Chemistry, University Museum, Oxford
1900		‖Ichioka, Tajiro, Prof., Minamihara, Hiratsuka, Japan
1888		Idris, Thomas Howell Williams, M.P., 120, Pratt-street, Camden Town, N.W.
1907	Trans.	Ingham, Harry, M.Sc. (Vict.), Grammar School, Chesterfield
1889	Trans.	‖Ingle, Herbert, B.Sc. (Leeds), F.I.C., 51, Cliff-road, Headingley, Leeds
1901	Trans.	‖Inglis, John Kenneth Harold, Prof., D.Sc. (Edin.), M.A., and B.Sc. (N.Z.), F.I.C., University of Otago, Dunedin, New Zealand
1901		Ingram, Beresford, M.A. (Cantab.), Education Offices, London County Council, Victoria Embankment, W.C.
1897	Trans.	Innes, William Ross, D.Sc. (Vict.), Ph.D. (Heidelberg), F.I.C., 19, St. James'-avenue, Cricklewood, N.W.
1901		‖Ionides, Stephen Archigenes, B.A. (Oxon.), 802, Equitable-building, Denver, Colo., U.S.A.
1908	Trans.	Irvine, James Colquhoun, Prof., D.Sc. (St. Andrews), Ph.D. (Leipzig), Chemical Laboratory, The University, and Edgecliff, St. Andrews
1915		Irving, George Stanley, 36, Red Rock-street, West Derby-road, Liverpool
1906		‖Irving, Henry Carlyle, B.A. (Oxon.), 2, High-street, Chingford, N.E.
1883		‖Irwin, Wilfred, Derwent Lodge, Cockermouth
1892		‖Isaac, John F. V., M.A. (Oxon.), 38, Silver-crescent, Gunnersbury, W.
1885		Ivatt, Albert, M.A. (Cantab.), The Engadine, Histon, Cambridge
1914		Iyer, Manappadam Ramaswami Viswanatha, Office of the Planting Expert, 25, South-parade, Bangalore, India
1894		Jackman, Edwin James, 60, Belgrave-road, Ilford, Essex
1883		‖Jackson, Alfred Henrick, Prof., B.Sc. (Vict.), M.Inst.E.E., The Electrical Engineering School, 349, Collins-street, Melbourne, Australia
1894	Trans.	Jackson, David Hamilton, M.A. and B.Sc. (N.Z.), Ph.D. (Heidelberg), 95, Abbey-road, N.W.
1907		Jackson, Ernest Wilfrid, Godrevy, Saltburn-by-the-Sea
1916		Jackson, Frederick William, B.Sc. (Lond.), A.C.G.I., The Laurels, Langley Green, Birmingham

Date of Election.			
1884	Trans.		Jackson, Herbert, Prof., F.I.C., Chemical Laboratory, King's College, Strand, W.C.
1909			Jackson, Robert Ernest, Tyneholme, Dartford
1892			‖Jackson, Samuel, A.R.C.S., F.I.C., 3, Buckingham-gardens, Perambore Barracks, N. Madras, India
1902			Jackson, William Brannan, Avalon, Balloch
1903			Jackson, William Henry, Violet Villa, Middleton St. George, Co. Durham
1910			Jacobs, Lionel Leslie, c/o Algoma Steel Corporation, Saulte Ste. Marie, Ont., Canada
1887			‖Jadhava, Khasberao Bhagawantrao, M.R.A.C., Mehsana, near Gujarat, India
1900			Jaffé, Adolf, 8, Leyburn-grove, Shipley
1878	Trans.		Jago, William, Barrister-at-Law, F.I.C., 1, Garden-court, Temple, E.C. ; and 17, Wilbury-avenue, Hove, Sussex
1912			Jamas, Ardesir Naserwanji Peston, M.A. and B.Sc. (Bombay), Jaifal-terrace, Forjet-street, Grant-road, Bombay, India
1912			James, Charles, New Hampshire College, Durham, N.H., U.S.A.
1914	Trans.		James, Dan Ivor, M.A. (Cantab.), B.Sc. (Wales), 19, White's-view, Bradford
1912			James, Edward Lewis, Holly Lodge, Larkhall-rise, Clapham, S.W
1912			James, Edwin Oliver, B.Sc. (Lond.), Rev., Dovedale, Wytham-street, Oxford
1916			James, George, 56, Cranworth-street, Chorlton-on-Medlock, Manchester
1904	Trans.		James, Thomas Campbell, M.A. (Cantab.), B.Sc. (Wales), Edward Davies' Chemical Laboratories, University College of Wales, Aberystwyth
1901	Proc.		Jamieson, James Sprunt, F.I.C., Government Laboratory, Durban, Natal, S. Africa
1879	Trans.	C.1882-5 F.S. 85-91 V.P.95-9, 1915–	†‖Japp, Francis Robert, Prof., M.A. and Hon. LL.D. (St. Andrews), F.R.S., F.I.C., 36, Twyford-avenue, West Acton, W.
1910	Trans.		Jaques, Arthur, D.Sc. (Dun.), F.I.C., 37, Sandringham-road, Waterloo, Liverpool
1902			Jardin, David Smith, A.R.C.S.I., F.I.C., Lynwood, Dundrum, Co. Dublin
1902			Jardine, Douglas Kennedy, B.Sc. (Vict.), The Glenan, John-street, Helensburgh
1882			Jarmay, Gustav, F.I.C., Hartford Lodge, Hartford, Cheshire
1905	Proc.		Jarrard, William John, B.Sc. (Lond.), A.R.C.S., The University, Sheffield

† Longstaff Medallist, 1891.

Date of Election.		
1896	Proc.	Jeffers, Ernest Haynes, 87, Kyrle-road, West-side, Clapham Common, S.W.
1909		Jeffery, John Hugh, 10, Daysbrook-road, Streatham Hill, S.W.
1911		Jenkin, William Alfred, Bella-vista 12, Rio Tinto, Provincia de Huelva, Spain
1891	Trans.	Jenkins, Henry Charles, Wh.Sc., A.R.S.M., Assoc. M.Inst.C.E., 804, Salisbury House, London Wall, E.C.
1904		Jenkins, Herbert, 19, Bank-street, Braintree
1892		‖Jenkins, John H. B., Chemical Laboratory, Great Eastern Railway Works, Stratford, E.
1910		Jenkins, Leslie Charles Wood, 26, Ulundi-road, Blackheath, S.E.
1906	Trans.	Jenkinson, Ernest Arthur, B.Sc. (Lond.), A.R.C.S., 1, Weston-road, Strood, Rochester
1894		Jenks, Robert Leonard, A.C.G.I., F.I.C., Custom House, Calcutta, India
1914		Jennings, John Cyril, Rosindell, Fairlop-road, Leytonstone, N.E
1897	Trans.	‖Jordan, David Smiles, M.A. (Glas.), D.Sc. (Vict.), Ph.D. (Heidelberg), Temora, Colinton, Midlothian
1912		Jewell, William, A.I.C., 8, Tower-road, Dartford
1879		Jewson, Francis Albert Bowen, F.I.C., 38A, Brixton-road, Stockwell, S.W.
1912	Trans.	Jobling, Edgar, B.Sc. (Lond.), A.R.C.S., 26, Doughty-street, Mecklenburgh-square, W.C.
1901		Johnson, Charles Harold, M.D., C.M., F.R.C.S. and M.R.C.P. (Edin.), Kerang, Victoria, Australia
1908		Johnson, Grove, 21, Murphy-street, Richmond, Melbourne, Australia
1883		Johnson, James Edward, F.I.C., 133, Earlham-grove, Forest Gate, E.
1904		Johnson, John Richard, Casita, Glencairn-road, Streatham Common, S.W.
1913	Proc.	Johnson, William, B.Sc. (Leeds), Walton, Stoneygate-avenue, Leicester
1904		Johnston, John Haslam, M.Sc. (Vict.), F.I.C., 8, Leopold-road, Wimbledon, S.W.
1896		Johnstone, James, F.I.C., Brachead, Parkhill, Rutherglen
1903		Jones, Alfred Owen, A.I.C., 48, Seymour-road, Bishopston, Bristol
1907		Jones, Benjamin Owen, Boksburg, Transvaal, S. Africa
1905	Trans.	Jones, Bernard Mouat, M.A. (Oxon.), 10, Carlyle-square, Chelsea, S.W.
1898		Jones, Edward, B.Sc. (Lond.), F.I.C., 15, Macaulay-road, Clapham, S.W.
1912		Jones, Edgar Dingle, 157, Wakehurst-road, Clapham Common, S.W.

Date of Election.			
1916			Jones, Edward Owen, B.Sc. (Wales), 16, Stuart-road, Acton, W.
1871	Trans.		Jones, Edward William Taylor, F.I.C., The Oaklands, and 10, Victoria-street, Wolverhampton
1873	Trans.		‖Jones, Francis, M.Sc. (Manc.), F.R.S.E., 17, Whalley-road, Whalley Range, Manchester
1894			‖Jones, George Cecil, A.C.G.I., F.I.C., 43, Great Tower-street, E.C.
1893			Jones, Hedley Gordon, F.I.C., 32, Beechhill-road, Eltham, S.E.
1876	Trans.		‖Jones, Henry Chapman, F.I.C., 67, Shakespeare-road, Hanwell, W.
1909			Jones, Henry Humphrys, 18, Colquitt-street, Liverpool
1913			Jones, Hilton Ira, Prof., Dakota Wesleyan University, Mitchell, S. Dakota, U.S.A.
1904			Jones, Horace Francis, Rose Bank, Cambridge-road, Uxbridge
1890			Jones, John Archyll, B.Sc. (Lond.), Reethville, Park-road, West Hartlepool
1901			Jones, John Lloyd Thomas, Col., I.M.S., M.B. (Dun.), M.R.C.S. (Eng.), D.P.H. (Cantab.), His Majesty's Mint, Bombay, India
1892	Trans.		Jones, Lionel Manfred, B.Sc. (Lond.), Municipal Technical School, Suffolk-street, Birmingham
1906			Jones, Llewelyn Thomas, B.Sc. (Wales), Sunnyside, Tyrfran, Llanelly
1891			‖Jones, Moses William, Stone Beck, Brislington, Bristol
1901			Jones, Robert Henry, M.Sc. (Viet.), The Harris Institute, Preston
1904			Jones, William App, A.M. (N. Carolina), Ph.D. (Baltimore), c/o The Boston Artificial Leather Co., 200, Fifth-avenue, New York City, U.S.A.
1910	Trans.		Jones, William Jacob, M.Sc. (Wales), 4, Beverley-road, Chiswick-lane, Chiswick, W.
1904	Trans.		‖Joseph, Alfred Francis, Prof., D.Sc. (Lond.), A.R.C.S., 296, Willesden-lane, N.W.
1911			Joseph, Edward Lionel, 96, Victoria-street, S.W.
1915			Joshi, Lemuel Lucas, M.D. (Cornell), B.Sc. (Bombay), Municipal Office, Bombay, India
1893	Trans.	C. 1906-09	Jowett, Hooper Albert Dickinson, D.Sc. (Lond.), 5, Miskin-road, Dartford
1900			Joyce, Thomas Goode, B.Sc. (Lond.), F.I.C., Lyttleton Preserve and Drysaltery Works, Bromford-lane, West Bromwich
1913			Kanga, Darab Dinsha, M.A. (Bombay), Elphinstone College, Bombay, India
1914			Kaufmann, George von, Christ's College, Cambridge

Date of Election.			
1886	Trans.		Kawakita, Michitada, Engineering College, Tokio, Japan
1905	Trans.		Kay, Sydney Alexander, D.Sc. (St. Andrews), Chemistry Department, The University, Edinburgh
1881	Trans.		‖Kay, William Edward, 349, The Cliff, Broughton, Manchester
1907	Trans.		Kaye, John, M.A. and B.Sc. (Glas.), North Britain Glass Works, Perth
1886	Trans.	C. 1903-5	‖Keane, Charles Alexander, D.Sc. (Vict.), Ph.D. (Erlangen), F.I.C., The Sir John Cass Technical Institute, Jewry-street, Aldgate, E.C.
1882			‖Keen, Austin, Hon. M.A. (Cantab.), Cefn Llys, Bentley-road, Cambridge
1912			Keenan, Thomas John, 751, East Nineteenth-street, Brooklyn, N.Y., U.S.A.
1908			Keiller, Patrick Anderson, B.Sc. (St. Andrews), c/o Colombo Commercial Co., Ltd., Colombo, Ceylon
1894			‖Kellas, Alexander Mitchell, B.Sc. (Lond.), 4, St. Mark's-crescent, Regent's Park, N.W.; and Chemical Dept., Middlesex Hospital Medical School, Cleveland-street, W.
1913			Keller, Douglas Rayment, B.Sc. (Lond.), A.C.G.I., c/o The Bromley Mantle Co., Weston-street, Bromley-by-Bow, E.
1874			Kellner, William, Ph.D. (Göttingen), F.I.C., 135, Victoria-road, Old Charlton, Kent
1882			‖Kemp, William Joel, F.I.C., Gypsum Mines, Ltd., Mountfield, Robertsbridge, Sussex
1903			Kemp-Welch, Maurice, B.A. (Cantab.), 4, Pollards Hill West, Norbury, Streatham, S.W.
1884			Kendall, George Frederic, B.A. (Cantab.), The Hollies, Stratford-on-Avon
1915	Trans.		Kendall, James, D.Sc., Chemistry Department, Columbia University, New York City, U.S.A.
1874			Kendall, James Alfred, F.I.C., Lonesome Chemical Works, Streatham Common, S.W.
1910	Trans.		Kenner, James, Ph.D. (Heidelberg), D.Sc. (Lond.), c/o Messrs. Chance and Hunt, Ltd., T.W.D., Trinity-street, Oldbury, Birmingham
1896			‖Kennicott, Cass Langdon, Chicago Heights, Illinois, U.S.A.
1903			Kent, Thomas Oliver, Handforth Laboratories, Handforth-road, Kennington, S.E.
1889			Kenwood, Henry Richard, M.B. and C.M. (Edin.), L.R.C.P. (Lond.), 126, Queen's-road, Finsbury Park, N.
1908	Trans.		Kenyon, Joseph, D.Sc. (Lond.), F.I.C., School of Chemistry, University Museum, Oxford
1915			Kernot, Joseph Charles, D.Chem. (Naples), 61, St. George's-terrace, Jesmond, Newcastle-on-Tyne

Date of Election.			
1903			Keir, James Stewart, A.R.C.S., F.I.C., 19, Reservoir-road, Edgbaston, Birmingham
1883			Kerry, William Hugh Rubens, The Sycamores, Windermere
1900			Kershaw, James Henry, Corporation Sewage Works, Dalton, Rotherham, Yorks.
1901			Kettle, James David, B.Sc. (Lond.), F.I.C., 17, Herndon-road, Wandsworth, S.W.
1902			Kewley, James, M.A. (Cantab.), Cambrian Lodge, Portishead, Bristol
1911			Khosla, Sant Ram, near Kotwah City, Lahore, India
1903			Kin, Thein, B.A. (Calcutta), Chemical Examiner's Office, Rangoon, Lower Burma, India
1872	Trans.	C. 1887-92	‖Kinch, Edward, Prof., F.I.C., Komaba, Haslemere, Surrey
1907	Trans.		King, Albert Theodore, B.Sc. (Lond.), F.I.C., 39, Kenilworth-avenue, Wimbledon, S.W.
1881	Trans.		King, Alfred John, Elleray, Windermere
1902			‖King, Frank Eustace, B.Sc. (Lond.), F.I.C., 75, Gracechurch-street, E.C.
1903			King, Frank William George, 127, Elborough-street, Southfields, Wandsworth, S.W.
1914	Trans.		King, George, M.Sc. (Birm.), A.I.C., 25, Whitmore-road, Small Heath, Birmingham
1911	Trans.		King, Harold, M.Sc. (Wales), Wellcome Chemical Research Laboratories, King-street, Snow Hill, E.C.
1897			‖King, Herbert, M.Sc. (Vict.), F.I.C., 102, Cross Flatts-avenue, Leeds
1876			King, John Falconer, F.I.C., 43, Stirling-road, Edinburgh
1902			King, Sidney Isaac, Arnside, Burnham, Somerset
1895			Kingdon, George Holman, M.A. (Oxon.), c/o Messrs. Crosfield, Ltd., Warrington; and Hill Crest, Frodsham, Warrington
1872	Trans.		‖Kingzett, Charles Thomas, F.I.C., Maplin, Frinton-on-Sea, Essex
1891	Trans.	C. 1894-6 V.P. 1908-1911	†‖Kipping, Frederic Stanley, Prof., D.Sc. (Lond.), Ph.D. (Munich), F.R.S., F.I.C., University College, Nottingham
1916			Kipping, Stanley Percival, Chalcots, 41, Roxborough-park, Harrow
1886			Kirby, Herbert Edward, Newman House, Belton-road, Willesden Green, N.W.
1909			Kirby, Oswald Farquhar, M.A. and B.Sc. (Aberd.), The Triangle, Oudtshoorn, Cape Colony, S. Africa
1895			‖Kirkaldy, Patrick Henry, Prof., F.I.C., Chemical Department, King's College, Strand, W.C.
1903			Kirkby, William, M.Sc. (Manc.), Winster House, Thornfield-road, Heaton Moor, Stockport

† Longstaff Medallist, 1909

Date of Election.		
1913		Kirkland, Thomas James, Rev., B.Sc. (Lond.), Hereward Hall, Ely
1889		Kitchin, John, The Middlesex Hospital, W.C.
1915		‖Kitto, William, 366, City-road, E.C.
1888		‖Knaggs, Alfred Battye, c/o Dr. Knaggs, Oak House, New North-road, Huddersfield
1910	Proc.	Knecht, Edmund, Prof., M.Sc. Tech. (Manc.), Ph.D. (Zürich), F.I.C., Beech Mount, Marple, Stockport
1903		Knight, Harley Fancut, F.I.C., 14, Old Queen-street, Westminster, S.W.
1896		Knight, John Burnett, Biskra, Malford-grove, South Woodford, N.E.
1910	Trans.	Knight, William Arthur, M.A. (Cantab.), B.Sc. (Lond.), D.Sc. (Bristol), Thuja Cottage, Marlborough
1878		Knights, James West, F.I.C., County Laboratory, Cambridge
1879		Knowles, Joshua, c/o J. H. Greenhalgh, Esq., Bingswood Printing Co., Ltd., Whaley Bridge, Stockport
1912		Knox, Archibald, 18, Newhall-terrace, Greenhead, Glasgow
1864		Knox, George Walter, B.Sc. (Lond.), Spencer House, South-place, Finsbury-pavement, E.C.
1887	Trans.	Koga, Yoshimasa, The Imperial Mint, Osaka, Japan
1914	Trans.	Kolhatker, Gopal Balkrishn, Prof., M.A. (Bombay), Ferguson College, Poona, India
1912		Komatsu, Shigeru, Institute of Chemistry, Imperial University, Kyoto, Japan
1904	Trans.	Komppa, Gustav, Prof., Ph.D. (Helsingfors), Polytechnik, Helsingfors, Finland
1885		Koningh, . Leonard de, F.I.C., 162, Shepherd's Bush-road, Hammersmith, W.
1910	Trans.	Krall, Hans, B.A. (Dub.), A.I.C., Mahommedan Anglo-Oriental College, Aligarh, U.P., India
1908	Proc.	Krishnayya, H. V., B.A. (Madras), Government Chemical Laboratory, Mallesvaram, Bangalore, Mysore, India
1913		Kur, Emmanuel Francis, c/o The British Hydron Co., Chald Lane Colour Works, Wakefield
1915		Kurnakov, Nikolai Semenovitsch, Prof., Institute of Mining, Petrograd, Russia
1916		Kursanov, Nikolai Ivanovitsch, Imperial Technical School, Moscow, Russia
1859	Trans.	Kynaston, Josiah Wyckliffe, F.I.C., Chemical Laboratory, 3, Oak-terrace, Beech-street, Liverpool
1900		Kynaston, William Charles Robert, 9, Harland-road, Higher Tranmere, Birkenhead

Date of Election.			
1912			Lacey, Edwin Charles, St. Julian's Lodge, West Norwood, S.E.
1906			Ladell, William Richard Simpson, F.I.C., 1, Worbeck-road, Anerley, S.E. ; and 104, Birch-lane, Manchester
1909			Lakhani, Hassum Alidina, M.D. (Brussels), Murud Janjira, Bombay Presidency, India
1893			Lamb, Edmund George, M.A. (Oxon.), M.P., Borden Wood, Liphook, Hants.
1900			Lamb, Morris Charles, The Leathersellers Technical College, 176, Tower Bridge-road, S.E.
1910			Lamb, Samuel, A.R.S.M., 22, Thynne-street, West Bromwich
1892	Trans.		‖Lamb, Thornton Charles, Ph.D. (Heidelberg), c/o Messrs. Brunner, Mond and Co., Crescent Wharf, Silvertown, E.
1910	Trans.		Lambert, Bertram, M.A. (Oxon.), Chemical Dept., University Museum, Oxford
1893			Lambert, Wesley J., 41, Bromley-road, Catford, S.E.
1912			Lampitt, Leslie Herbert, M.Sc. (Birm.), Bowyer-road, Alum Rock, Birmingham
1903	Proc.		Lamplough, Francis Edward Everard, M.A. (Cantab.), Trinity College, and Storey's-way, Cambridge
1875			Lancaster, William James, F.R.C.S., J.P., Santa Margherita, Torquay
1902	Proc.		Landau, A. Lionel, 24, Leigh-road, Highbury Park, N.
1900	Trans.		Lander, George Druce, D.Sc. (Lond. and St. Andrews), F.I.C., Royal Veterinary College, Camden Town, N.W.
1897	Trans.		Lang, William Robert, Prof., D.Sc. (Glas.), F.I.C., The University, Toronto, Canada
1899			Lange, Ernest Frederick Stephen, c/o Messrs. Beyer, Peacock & Co., Ltd., Gorton Foundry, Manchester
1885			Langer, Charles, Ph.D. (Zürich), Ynyspenllwch, Clydach, Glam.
1891			‖Langham, Edgar Norman, Rev., M.A. (Cantab.), Rastrick Grammar School, Brighouse
1912	Trans.		Langton, Harold McKee, B.A. (Cantab.), B.Sc. (Lond.), Milton, Aylestone-road, Cambridge
1912	Trans.		Lankshear, Frederick Russell, B.A. (N.Z.), M.Sc. (Manc.), The University, Manchester
1894	Trans.	C. 1904–7 V.P. 1916–	Lapworth, Arthur, Prof., D.Sc. (Lond.), F.R.S., F.I.C., The University, Manchester
1908			Larmuth, Lionel Gordon, Gaythorn, Hazel-grove, Stockport
1901	Trans.		Lattey, Robert Tabor, St. Paul's Vicarage, Tiverton
1906			Lattey, William Tabor, Tarmon, Streatham Park, S.W.
1891	Trans.		‖Lauder, Alexander, D.Sc. (Edin.), F.I.C., Edinburgh and East of Scotland College of Agriculture, 13, George-square, Edinburgh

Date of Election.		
1886	Trans.	Laurie, Arthur Pillans, Prof., M.A. (Cantab.), D.Sc. (Edin.), F.R.S.E., The Heriot-Watt College, Edinburgh
1910		Lavender, John Herbert, The Laboratory, Messrs. E. G. Wrigley & Co., Ltd., Foundry Lane Works, Soho, Birmingham
1876		‖Law, Channell, The Museum, Torquay
1905	Trans.	Law, Herbert Drake, D.Sc. (Lond.), Castle Fields, Rastrick, Brighouse
1896		‖Law, Herbert Edward, R.F.D., No. 1, Redwood City, Cal., U.S.A.
1890	Trans.	‖Law, Robert, Major, F.I.C., The Royal Mint, Melbourne, Australia
1903		Lawrence, Henry William, Johnsonville, Wellington, New Zealand
1882		Laws, Joseph Parry, F.I.C., Laurel Bank, Claremont-road, Headingley, Leeds
1913		Lawson, Joseph Stuart, 10, Bush-lane, Cannon-street, E.C.
1916		Laxton, Frank Charles, High-street, Ely
1886		‖Leach, Walter, 21, St. Andrew's-place, Bradford
1902		Leader, George Herbert, Montego Bay Secondary School, Montego Bay, Jamaica
1894	Trans.	‖Lean, Bevan, B.A. and D.Sc. (Lond.), Sidcot School, Winscombe, Somerset
1888		Lease, Frank Edward, Sapong Estate, Fort Birch, British North Borneo
1902		Leather, John Petty, Whittier, Colne-road, Burnley
1891	Trans.	Leather, John Walter, Major, V.D., F.I.C., c/o Messrs. Grindlay & Co., 54, Parliament-street, S.W.
1900		‖Leathes, John Beresford, Prof., M.A., M.B. and B.Ch. (Oxon.), F.R.C.S. (Eng.), F.R.S., The University, Sheffield
1889		Ledingham, Laurence Napier, Govandale, Taptonville-crescent, Sheffield
1915		Lee, John William, Belmont, Hasland, Chesterfield
1897	Trans.	‖Lee, Theophilus Henry, Servizo Geologico e Mineralogico do Brazil, Ministeria de Agricultura, Rio de Janeiro, Brazil
1909		Leech, Benjamin, M.A. (Cantab.), Beech Knoll, Macclesfield
1910		Leechman, Alleyne, M.A. (Oxon.), Department of Science and Agriculture, Georgetown, Demerara, British Guiana
1905		Leek, William Henry, B.A. (Lond.), Brookwood, Leigh
1903	Trans.	Lees, Frederic Herbert, F.I.C., 31, Summerhill-road, Dartford
1913	Trans.	Lefebure, Victor, B.Sc. (Lond.), 49, Craford-road, Tufnell Park, N.
1889		‖Legg, John Edmund, M.A. (Cantab.), F.I.C., Cae Rhys, Dorchester-road, Weymouth
1901		Lehmann, Adolf Ludwig Ferdinand, B.Sc. (Toronto), Ph.D. (Leipzig), University of Alberta, Strathcona, Alberta, Canada
1914		Leigh, Alfred John, B.Sc. (Lond.), A.R.C.S., Duff House, Banff

Date of Election.			
1889			Leigh, Cecil, F.I.C., Birmingham Metal and Munitions Co., Ltd., Adderley Park Rolling Mills, Birmingham
1914			Leighton, Frederic William, Lydiard Tregoze, Wootton Bassett, Swindon
1914			Leighton, John Orron, 30, Albany-street, Hull
1913			Leitch, Peter Thomas, 3, Kitson-road, Barnes, S.W.
1913			Leivesley, Sidney Oliver, 11, Eric-street, Leichhardt, Sydney, N.S.W.
1916			Lelean, Philip, Major, R.A.M.C., F.R.C.S., D.P.H., 37, Primrose Mansions, Battersea Park, S.W.
1904			Le May, Percy Kent, 68, Gainsford-street, Horsley Down, S.E.
1912			Lenfestey, Harold John de Quetteville, 134, Waterloo-road, Wolverhampton
1891			Lennox, Robert Nicol, Morvah, Hartington-road, Chiswick, W.
1906	Trans.		Le Rossignol, Robert, B.Sc. (Lond.), A.I.C., Prinz Regentenstrasse 108, Berlin, W., Germany
1904			Lessing, Rudolf, Ph.D. (Munich), Southampton House, 317, High Holborn, W.C.
1902			‖Lessner, Charles, Carril, Spain
1895	Trans.	C. 1911-13	‖Le Sueur, Henry Rondel, Major, D.Sc. (Lond.), F.I.C., St. Thomas's Hospital, S.E.
1879	Trans.		Letts, Edmund Albert, Prof., Hon. D.Sc. (R.U.I.), Ph.D. (Göttingen), F.I.C., Queen's College, Belfast
1914			Levinstein, Herbert, M.Sc. (Vict.), Ph.D. (Zürich), Messrs. Levinstein, Ltd., Blackley, Manchester
1903			Levy, Henry Wolff, 423B, Little Collins-street, Melbourne, Australia
1914			Levy, Joseph Frederick, 26, Compton-terrace, Highbury N.
1909	Trans.		Levy, Leonard Angelo, M.A. (Cantab.), D.Sc. (Lond.), F.I.C., 26, Teignmouth-road, Cricklewood, N.W.
1912	Trans.		Levy, Stanley Isaac, B.A. (Cantab.), B.Sc. (Lond.), A.I.C., 9, Parkhurst-road, Holloway, N.
1907			Lewis, Carl, Lewis'-buildings, 255, President-street, Germiston, Transvaal, S. Africa
1916			Lewis, Edgar, Wainholm, Elkington-road, Burry Port, Carmarthenshire
1899	Trans.		Lewis, Edward Watkin, The Bower, Loughton, Essex
1901	Proc.		Lewis, Ernest Alfred, 310, Dudley-road, Birmingham
1910			Lewis, Frederick Charles, School of Pathology, Yates Laboratories, The University, Liverpool
1910	Trans.		Lewis, Samuel Judd, D.Sc. (Tübingen), B.Sc. (Lond.), F.I.C., The Laboratories, Staple Inn-buildings, High Holborn, W.C.
1909	Trans.		Lewis, William Cudmore McCullagh, Prof., M.A. (R.U.I.), D.Sc. (L'pool.), The University, Liverpool

Date of Election.			
1894	Trans.		Lewis, William Henry, M.A. (Oxon.), F.I.C., Royal Albert Memorial College, Exeter
1869	Trans.		‖Lewis, William James, Prof., M.A. (Oxon. and Cantab.), F.R.S., New Museums, Cambridge
1913			Lewis, William John, c/o Messrs. Keams, Allan & Co., Ltd., Baxenden, Accrington
1896			Lidgey, Cecil Rudolf, 45, Cresswell-road, East Twickenham
1900			Liebmann, Adolf, M.A. and Ph.D. (Bonn), The Whim, Weybridge
1903			Linday, John Howard, c/o The Nivalbo Co., Mapperley, Nottingham
1901			‖Linde, Harold Theodor Granville van der, c/o National Synthetic Co., Perth Amboy, N.J., U.S.A.
1899			Lindsey, Robert William, 1, Dartmouth-park-avenue, N.W.
1886	Trans.	C. 1911-13	Ling, Arthur Robert, F.I.C., 74, Great Tower-street, E.C.
1911			Ling, Herbert James, Hankow Dispensary, Hankow, China
1899			Linstead, Edward Flatman, 15, Roseneath-avenue, Winchmore Hill, N.
1905	Trans.		Lister, Joseph, B.Sc. (Lond.), Ph.D. (Leipzig), A.R.C.S., The Technical Institute, Tunbridge Wells
1853	Trans.	(V.P. 1883-7, 1893-1901.)	‖Liveing, George Downing, Emeritus Prof., M.A. (Cantab.), Hon. Sc.D. (Cantab. & Dub.), F.R.S., F.I.C., The Pightle, Cambridge
1872	Trans.	V.P. 1910-13	‖Liversidge, Archibald, Emeritus Prof., M.A. (Cantab.), Hon. LL.D. (Glas.), A.R.S.M., F.R.S., F.I.C., Fieldhead, Coombe Warren, Kingston-on-Thames
1903			Livesey, Charles Edwin Leonard, B.Sc. (Vict.), Bootham School, York
1883			Livingston, William John, F.I.C., 30, Fountayne-road, Stoke Newington Common, N.
1909			Livsey, Harry, 26, Thorpe-street, Old Trafford, Manchester
1880			‖Lloyd, Alfred, The Dome, Bognor, Sussex
1913			Lloyd, Daniel William, B.Sc. (Lond.), The Academical Institution, Coleraine, Co. Londonderry
1876	Trans.		Lloyd, Frederick James, F.I.C., 135, Queen's-road, Finsbury Park, N.
1913			Lloyd, Harold Charles, B.Sc. (Birm.), Central School, Llandudno
1907			Lloyd, Percival George, Kelvinside, Lower Ham-road, Kingston-on-Thames
1896			Lloyd, Thomas Henry, F.I.C., c/o Messrs. Quibell Bros., Ltd., Newark-on-Trent
1900			Lockhart, Thomas Lamb, 21, Abercorn-terrace, Portobello, Midlothian
1902			Logan, Thomas Stratford, L.R.C.P., L.R.C.S. (Edin.), D.P.H. (Lond.), Bucks County Asylum, Stone, Aylesbury
1912			Lomax, Ernest Lawson, M.Sc. (Manc.), c/o Anglo-Persian Oil Co., Ltd., Gresham House, 24, Old Broad-street, E.C.

Date of Election.			
1884			London, John Edward, M.D. (Dun.), M.R.C.S. (Eng.), L.R.C.P. (Lond.), 62, Main-street, Georgetown, Demerara, W. Indies
1872			‖Longstaff, George Blundell, M.A. and M.D. (Oxon.), F.R.C.P. (Lond.), M.R.C.S. (Eng.), Highlands, Putney Heath, S.W.
1904			Longstaff, James Patrick, D.Sc. (Edin.), Broadway Chambers, Westminster, S.W.
1873	Proc.		‖Loram, Herbert Yabsley, F.I.C., 49, Buxton-road, Chingford, Essex
1916			Lorenz, Hans Hugo Herbert, M.A. (Cantab.), Fairfield, Brockley Park, Forest Hill, S.E.
1882			Love, Edward Gurley, Ph.D. (Columbia), 130, East 15th-street, New York City, U.S.A.
1882			‖Lovibond, Thomas Watson, F.I.C., West Jesmond House, Newcastle-on-Tyne
1910			Low, Kenneth Stewart, A.R.S.M., 48, Rich-terrace, Earl's Court, S.W.
1910	Trans.		‖Lowe, Clement Ward, F.I.C., Thorneyholme, Knutsford
1904	Trans.		Lowe, Frank Harold, M.Sc. (Vict.), 4, Ranelagh-gardens, Hurlingham, S.W.
1878			‖Lowe, Walter Bezant, M.A. (Cantab.), Cae Carw, Llanfairfechan, Carnarvonshire
1876			Lowe, William Foulkes, A.R.S.M., F.I.C., 18, Hough-green, Chester
1898	Trans.	C. 1912-16	‖Lowry, Thomas Martin, D.Sc. (Lond.), F.R.S., 17, Eliot-park, Lewisham, S.E.
1901			Lowson, William, B.Sc. (Lond. and Leeds), F.I.C., The University, Leeds
1913			Loynes, Walter Cyril, Eastfield, Comberton-road, Kidderminster
1899			Lucas, Alfred, F.I.C., Survey Department, Finance Ministry, Giza, Egypt
1905			Lucas, Edward William, F.I.C., Oxford Works, Tower Bridge-road, S.E.
1902			Lucas, Harry, The South of England College of Pharmacy, 186, Clapham-road, S.W.
1911			Lucas, Thomas Riley, A.C.G.I., Bhubaneswar, Orissa, India
1912			Lucas, William Thornton, M.A. (Cantab.), 48, Rosebery-avenue, Westoe, South Shields
1905			Luck, Alfred Courtenay, San Martin 475, Buenos Ayres, Argentine, S. America
1910			Lucking, Hubert Leslie, Ph.D. (Heidelberg), A.I.C., Hardwick, Garrick-avenue, Golders Green, N.W.
1902	Trans.		Ludlam, Ernest Bowman, D.Sc. (L'pool.), M.Sc. (Vict.), 5, Chantry-road, Clifton, Bristol

Date of Election.		
1877	Trans.	‖Luff, Arthur Pearson, M.D., B.Sc., F.R.C.P. and L.S.A. (Lond.), M.R.C.S. (Eng.), D.P.H. (Glas.), F.I.C., 9, Queen Anne-street, Cavendish-square, W.
1915		Lumsden, Colin Henry, B.Sc. (Lond.), A.I.C., Homelea, Sandcliffe-road, Erith, Kent
1890	Trans.	Lumsden, John Scott, D.Sc. (St. Andrews), Ph.D. (Munich), 1 Somerville-place, West-park, Dundee
1907		Lunan, George, 50, Garscube-terrace, Murrayfield, Edinburgh
1909		Lundholm, Carl Olof, F.I.C., 33, Beulah-hill, Upper Norwood, S.E.
1872	Trans.	‖Lupton, Sydney, 102, Park-street, Grosvenor-square, W.
1893	Trans.	‖Luxmoore, Charles Mann, D.Sc. (Lond.), F.I.C., 49, Garden-avenue, Mitcham
1899		Luxton, Thomas, B.A. and B.Sc. (Lond.), 116, North Boulevard, Hull
1913		Lycett, Percival James, c/o Messrs. Chance & Hunt, Ltd., Government Dept., Site "A," Oldbury, Birmingham
1908		Lyell, Henry Robert, F.I.C., A.K.C., Redcott, Dacres-road, Forest Hill, S.E.
1908		Lynch, Gerald Roche, M.B. and B.S. (Lond.), L.M.S.S.A., 17, Upper Addison-gardens, Holland Park, W.
1886	Trans.	Lyons, Albert Brown, A.M. (Williams Coll.), M.D. (Mich.), 102, Algee-avenue, Detroit, Mich., U.S.A.
1888		Maben, Thomas, 20, Great Pulteney-street, W.
1915		Maben, Thomas Morison, 16, Battery-road, Singapore, Straits Settlements
1896		Macadam, Herbert Edwin, Odam's Wharf, Victoria Docks, E.
1888		‖Macadam, Stevenson John Charles George, F.I.C., Analytical Laboratory, 55, York-place, Edinburgh
1899		McAlley, James, 5, George-street, Falkirk
1903		Macara, Thomas, F.I.C., 20, Denton-road, Stroud Green, N.
1890		‖MacArthur, John Stewart, Loch Lomond Radium Works, Balloch, Dumbartonshire
1911	Trans.	McBain, James William, M.A. (Toronto), Ph.D. (Heidelberg), The University, and 71, Cotham-brow, Bristol
1913	Trans.	Macbeth, Alexander Killen, M.A. and B.Sc. (Q.U.I.), 3, Victoria-terrace, Cregagh, Belfast
1900		McCall, William, 13, Dargarvel-avenue, Dumbreck, Glasgow
1902		MacCallum, Douglas Archibald, Central-chambers, 93, Hope-street, Glasgow
1916		McCay, Leroy Wiley, The Library, Princeton University, Princeton, N.J., U.S.A.

Date of Election.		
1905		McCleary, William, 61, Station-road, Pendlebury, Manchester
1899		McClumpha, Robert, 372, Westgate-road, Newcastle-on-Tyne
1906	Trans.	McCombie, Hamilton, M.A. (Aberd.), B.Sc. (Lond.), Ph.D. (Strassburg), A.R.C.S., F.I.C., The University, Birmingham
1907	Trans.	McConnan, James, D.Sc. (L'pool.), M.Sc. (Vict.), Ph.D. (Jena), 8, Crosby-road-south, Waterloo, Liverpool
1904		McCourt, Cyril Douglas, A.C.G.I., 29, Criffel-avenue, Streatham Hill, S.W.
1899		‖McCracken, James, 40, Roxburgh-circus, Cardonald, Glasgow
1896	Trans.	McCrae, John, jun., Ph.D. (Heidelberg), F.I.C., Government Laboratories, P.O. Box 1080, Johannesburg, S. Africa
1899		McCreath, William Dunlop, Quantock Vale Cider Co., Ltd., North Petherton, Bridgwater
1890		‖McCubbin, William Alexander, F.I.C., Meeson House, Meeson, Wellington, Salop.
1897		MacCulloch, Charles, Bretton, Hamilton E., New Zealand
1894		McCutcheon, James, Meniehaus, Woodend-drive, Jordanhill, Glasgow
1903		Macdonald, David Baird, Krux Chemical Works, 33, Vulcan-road, Leicester
1901		Macdonald, F. G., Durban Roodeport Gold Mining Co., Ltd., P.O. Box 111, Roodeport, Transvaal, S. Africa
1894	Trans.	MacDonald, George William, M.Sc. (Melbourne), Whitefriars, Rochester
1912	Trans.	Macdonald, James Leslie Auld, B.Sc. (St. Andrews), 13, Howard-place, St. Andrews
1906		Macdonald, Thomas, c/o Messrs. Hollingshurst and Co., Taj Buildings, Hornby-road, Bombay, India
1891		MacDonald, William, A.R.C.S., A.R.S.M., F.I.C., Assistant Postal Secretary, Peking, China
1906		McDowall, John, c/o Sharouneh Phosphate Mines, Sebaieh Station, Upper Egypt
1910		McEvilly, Thomas Patrick Cheetham, P.O. Box 1164, Durban, Natal, S. Africa
1886		MacEwan, Peter, 64, Southwood-lane, Highgate, N.
1895		MacFarlane, Alexander, 42, Trefoil-gardens, Shawlands, Glasgow
1891		Macfie, Robert Andrew Scott, M.A. (Cantab.), B.Sc. (Edin.), 34, Moorfields, Liverpool
1910		MacGeorge, David Jackson, 2nd Lieut., 1/Xth Gurkha Rifles, Maymyo, Upper Burma
1895		McGlashan, John, P.O. Balapur Tolodi, Tehsil Brahamapuri, Dist. Chanda, C.P., India
1887	Trans.	McGowan, George, Ph.D. (Leipzig), F.I.C., 21, Montpelier-road, Ealing, W.

Date of Election.			
1908			MacGregor, Gregor, M.A. and B.Sc. (Glas.), Sinclairtownbank, Kirkcaldy, Fife
1893			McGregory, Joseph Frank, Prof., Colgate University, Hamilton, N.Y., U.S.A.
1914			Machin, Robert Ernest, B.Sc. (Lond.), 5, Redcliffe-road, S. Kensington, S.W.
1915			MacInnes, Ronald, 17, Shrewsbury-road, New Southgate, N.
1890			Macintyre, Alfred Edgar, Ph.D. (Jena), The Chemical Laboratory, Dominion Arsenal, Quebec, Canada
1914	Trans.		MacIvor, Ralph Waldo Emerson, F.I.C., c/o Metals Recovery, Ltd., 47, Victoria-street, Westminster, S.W.
1914	Trans.		McKee, James Lyttle, B.A. and M.Sc. (R.U.I.), Ph.D. (Freiburg), Internment Station, Amherst, Nova Scotia, Canada
1901	Trans.	C. 1910-13	‖McKenzie, Alexander, Prof., M.A. and D.Sc. (St. Andrews), Ph.D. (Berlin), F.R.S., Chemistry Department, University College, Dundee, and Annandale, Duntrune-terrace, Broughty Ferry, Forfarshire
1897	Trans.		Mackenzie, John Edwin, D.Sc. (Edin.), Ph.D. (Strassburg), 2, Ramsay-gardens, Edinburgh
1902			Mackenzie, John Ross, Worcester Brewery, Worcester
1899			‖Mackenzie, Thomas, 1, High-street, Inverness
1900			Mackenzie, Thomas Ebenezer, Mina da Serra da Careira, Grandola, Portugal
1893			McKerrow, Charles Alexander, 8, Berners-street Mansion, W.
1916			‖MacLachlan, Hugh Findley, Woodend, Styal, Manchester
1916			‖MacLachlan, James Baird, Rookswood, Broughton Park, Manchester
1915			MacLachlan, Thomas, 23, Clarendon-road, Lewisham, S.E.
1914			McLaren, Alexander Williamson, Ramsden Dock, Barrow-in-Furness
1897	Proc.		Maclaurin, James Scott, D.Sc. (N.Z.), Wellington, New Zealand
1868	Trans.	C 1871-4, 80-4, 95-9. V.P. 1887-90, 1901-04	‖McLeod, Herbert, Prof., Hon. LL.D. (St. Andrews), F.R.S., 37, Montague-road, Richmond, Surrey
1899			McLeod, James, F.I.C., Gas Works, Greenock
1903			MacMahon, Frederick William, Two Seven, The Crescent, New Southgate, N.
1879			‖Macmillan, James Laker, 9, Wool Exchange, MacQuarrie-place, Sydney, N.S.W.
1912			McMillan, William, c/o Messrs. Curtis, Campbell & Co., Plantation Non Pareil, Demerara, B.W.I.
1889	Trans.		‖McMurtry, George Cannon, A.R.S.M., A.R.C.S., Templemore, Richmond, Nelson, New Zealand

Date of Election.			
1912			McMyn, James William, Oakleigh, Manchester-road, Accrington
1880		C. 1915-16	Macnab, William, F.I.C., 10, Cromwell-crescent, S.W.
1885	Trans.		‖Macnair, Duncan Scott, Ph.D. (Würzburg), B.Sc. (Lond.), 67, Braid-avenue, Edinburgh
1913			Macnaughten, Duncan James, 31, Clonmel-road, Fulham, S.W.
1910			McNish, Malcolm, Ferndale, St. Neots
1914			Macpherson, Archibald, c/o Messrs. Menley & James, Ltd., Menley House, Farringdon-road, E.C.
1913			Mahamadi, Ghulam Ali, B.A. (Bombay), c/o Syed Fayazuddin, Esq., The Cawnpur Tannery, Bhanana Purwa, Cawnpore, U.P., India
1899			Main, Hugh, B.Sc. (Lond.), Almondale, Buckingham-road, South Woodford, N.E.
1900			‖Mair, William, 37, Morningside-drive, Edinburgh
1902	Trans.		Maitland, William, D.Sc. (Aberd.), Robert Gordon's Technical College, Aberdeen
1914			Maitra, Birendranath, M.Sc. (Calcutta), 4, Bakulbagan 1st-lane, Bhowanipur, Calcutta, India
1910			Majima, Rikō, Prof., D.Sc. (Tokio), Chemical Institute, Imperial University, Sendai, Japan
1906			Majumdar, Tarak Nath, 37, Lower Chitpore-road, Calcutta, India
1894			Makin, Charles James Shaw, F.I.C., 47, Vineyard-hill, Wimbledon Park, S.W.
1914			Makin, Frederick Arthur, The Nest, Taunton-road, Ashton-u-Lyne
1915			Mallannah, Sreenagula, M.D. and C.M. (Edin.), D.P.H. (Cantab.), H.H. The Nizam's Government, Hyderabad, Deccan, India
1885	Trans.		‖Mallet, Frederic Richard, F.I.C., 20, King's-avenue, Ealing, W.
1897			Mallinson, Willie Lee, Gawthorp-green, Kirkheaton, Huddersfield
1904			Mander, Alfred, Belle Vue House, Malvern
1903			Mander, Percy George, B.Sc. (Lond.), The Grammar School, Doncaster
1903			Mann, Ernest William, B.Sc. (Lond.), F.I.C., Lyndale, Northfield-road, King's Norton, Birmingham
1903			Mann, John Christopher, c/o Messrs. Robinson Bros., Ltd., Ryder's-green, West Bromwich
1902			Mann, William, B.Sc. (Lond.), 84, Inchmery-road, Catford, S.E.
1896			Manners, Hugh, M.A. and B.Sc. (Glas.), Academy House, Airdrie
1908			Mansfield, Herbert, B.Sc. (Lond.), F.I.C., 6, Aubrey-road, Crouch End, N.
1897			Mansford, Charles John Jodrell, B.A. (Lond.), The Grammar School, Dartford

Date of Election.			
1910			Marcan, Alexander, F.I.C., A.I.M.M., Samsen, Bangkok, Siam
1913			Marchant, Frank Clifford, St. Kilda's, Manor-road, Forest Hill, S.E.
1895			‖Marchant, Robert Charles, Salisbury-road, Andover
1905	Trans.		Marle, Ernest Robert, B.Sc. (Lond.), A.R.C.S., Omori, Bitterne, Southampton
1916	Trans.		Marsden, Arthur, Gas Co., Upper Bristol-road, Bath
1907	Trans.		Marsden, Herbert, B.Sc. (Manc.), Stable Hobba, Penzance
1915			Marsden, Kenneth George, B.A. (Oxon.), Culloden, Neboda, Ceylon
1895			Marsden, Prosper Henry, The Royal Infirmary, Liverpool
1883	Trans.	C. 1902-7	‖Marsh, James Ernest, M.A. (Oxon.), F.R.S., University Museum, Oxford
1895	Trans.		Marshall, Arthur, A.C.G.I., F.I.C., Waverley Cottage, Naini Tal, India
1887			‖Marshall, William, F.I.C., Laboratory, Ladybrook-road, Cheadle Hulme, Stockport
1897			Martin, Charles Henry, 50, Longmead-road, Claremont, Pendleton, Manchester
1902			Martin, Francis, 5, Priestlands Park-road, Sidcup, Kent
1906			Martin, Frederick James, c/o The Bundi Tin Mining Syndicate, Bundi, Kemaman, viâ Singapore, Straits Settlements
1911	Trans.		Martin, Geoffrey, Ph.D. (Rostock), M.Sc. (Bristol), B.Sc. (Lond.), 21, Hamilton-crescent, Palmer's Green, N.
1906			Martin, George Frederick Wesley, 14, Castle-park, Lancaster
1898	Trans.		‖Martin, George Herbert, M.A. (Oxon.), The Grammar School, Bradford
1907	Trans.		Martin, Gerald Hargrave, 2, Cintra Park Mansions, Church-road, Upper Norwood, S.E.
1885			‖Martin, Gerald Ward, Lieut.-Col., 8, Petersham-terrace, Gloucester-road, S.W.
1913			Martin, Henry Stephen, 64, Dyke-road, Brighton
1910			Martin, William Ernest, 111, Bellevue-road, Berea, Durban, Natal, S. Africa
1909			Martin, William George, B.Sc. (Wales), Fellside, Hexham
1902			Martindale, William Harrison, Ph.D. (Marburg), 10, New Cavendish-street, W.
1871			‖Martineau, George, Gomshall Lodge, Gomshall, Guildford
1887			‖Martineau, Sydney, Streatham-grove, Norwood, S.E.
1912			‖Masani, Nadirshaw Adarji, Prof., M.A. and B.Sc. (Bombay), Baroda College, Baroda Camp, India
1898			Mascarenhas, John Charles, Ph.D. (Coimbra), 40, Broad-street House, E.C.
1905			Mason, Arthur Walter, B.Sc. (Lond.), 118, Aldeburgh-road, Leiston, Suffolk

Date of Election			
1915	Trans.		Mason, Frederick Alfred, B.A. (Oxon.), Ph.D. (Munich), 21, Queen-square, W.C.
1915	Proc.		Mason, John Ernest, B.Sc. (Lond.), 3, Woodpath, Southsea, BO., Portsmouth
1882	Trans.		Masson, David Orme, Prof., M.A. and D.Sc. (Edin.), F.R.S., The University, Melbourne, Australia
1910	Trans.		Masson, James Irvine Orme, M.Sc. (Melb.), Research Department, Royal Arsenal, Woolwich, S.E.
1897			Masters, Edward, B.Sc. (Lond.), A.R.C.S., Rock Mount, 197, Hinckley-road, Leicester
1906			Mastin, John, M.A., D.Sc., Ph.D., Litt.D., LL.D., Kenyon Hall, Kenyon, Manchester
1909			Matchett, Andrew Sneddon, 13, Bute-gardens, Cathcart
1916			Mather, Wilfred, Jessamine Cottage, Audenshaw, Manchester
1904			Mathews, Harold Joseph Clarke, Massey's Burnley Brewery, Ltd., Burnley
1902			Mathieson, Robert, J.P., Rill Bank, Innerleithen, Peeblesshire
1876	Trans.		‖Matthews, Charles George, F.I.C., Abendberg, 31, Stapenhill-road, Burton-on-Trent
1916			Matthews, Donald John, c/o The Marine Biological Association, Plymouth
1880	Trans.	C. 1906-09	‖Matthews, Francis Edward, Ph.D. (Göttingen), F.I.C., Ash Lawn, The Glebe, Blackheath, S.E.
1884			‖Matthey, Edward, Col., C.B., A.R.S.M., 31A, Weymouth-street, W.
1893			‖Mawer, William Frederick, 27, Cathles-road, Balham, S.W.
1912			Maxwell, Francis, Ph.D. (Heidelberg), 77, Lawrie Park-road, Sydenham, S.E.
1913			Maxwell, Marius, 77, Lawrie Park-road, Sydenham, S.E.
1913			May, Joseph Horsnell, M.I.E.E., 21, Donovan-avenue, Muswell Hill, N.
1909	Trans.		May, Percy, D.Sc. (Lond.), 126, Cazenove-road, Stamford Hill, N.; and Organic Chemical Laboratory, South Parks-road, Oxford
1999			May, Roland Josiah, Powerscroft, Grange-gardens, Southend-on-Sea
1913			Maynard, Harry Bertram, c/o The Pacific Phosphate Co., Ltd., Ocean Island, Western Pacific, via Sydney, N.S.W.
1892			Meacham, Charles Stephen, c/o Messrs. Ohlsson's Cape Breweries, Ltd., Newlands, Cape Town, S. Africa
1910	Trans.		Meanwell, Charles Wright, F.I.C., 15, Woodlands-crescent, Muswell Hill, N.
1904			Mears, Francis D'Oyley, jun., c/o The Campbell Ehrenfried Co., Ltd., Auckland, New Zealand

Date of Election.			
1901	Trans.		Mees, Charles Edward Kenneth, D.Sc. (Lond.), 55, Huntington-park, Rochester, N.Y., U.S.A.
1908			Meggitt, Alfred Ash, B.Sc. (Lond.), Agricultural Chemist, Jorhat, Assam, India
1896			Meggitt, Loxley, F.I.C., c/o C.W.S., Ltd., Wheatsheaf Works, Alexandria, Sydney, N.S.W.
1913			Mehta, Bhaichand Anupchand, M.A. (Bombay), c/o Messrs. Karsonji Mulchand, Rajkote, Kathiawad, India
1912			Meister, Frederick James, 1, Stanley-terrace, Alva, Clackmannanshire
1905	Trans.		Meldrum, Andrew Norman, Prof., D.Sc. (Aberd.), College of Science, Ahmedabad, Bombay, India
1894			Melland, Godfrey, M.Sc. (Vict.), A.R.S.M., F.I.C., Chemical Department, The Polytechnic, Woolwich, S.E.
1908			Melling, Samuel Ernest, F.I.C., The Cliff, Higher Broughton, Manchester
1914	Trans.		Mellor, Benjamin Stanley, M.Sc. (Manc.), 70, Ardrossan-road, Saltcoats, BO., Ayrshire
1902	Trans.		Mellor, Joseph William, D.Sc. (N.Z.), Sandon House, Regent-street, Stoke-on-Trent
1875			‖Melmore, Pattinson Banks, North How, Maryport
1912			Menon, Ambat Kesava, B.A. (Madras), Chittur-Cochin, S. Malabar, Madras Presidency, India
1900	Proc.		Menzies, Alan Wilfrid Cranbrook, Prof., M.A. and B.Sc. (Edin.), Ph.D. (Chicago), Princeton University, New Jersey, U.S.A.
1912			Menzies, Robert Charles, c/o Messrs. A. Boake, Roberts & Co., Ltd., Carpenters-road, Stratford, E.
1889			‖Mercer, Thomas, F.I.C., 31, Gwdyr Mansions, Hove, BO., Brighton
1901			Meredith, William, 63, Albion-place, Ulverston, Lancs.
1896			Merrett, William Henry, A.R.S.M., F.I.C., Hatherley, Grosvenor-road, Wallington, Surrey
1908			Merrick, Arnold, B.Sc. (Dun.), 66, Rothbury-terrace, Newcastle-on-Tyne
1891			Merrils, Frederick Johnson, Haxworth-chambers, 25, Figtree-lane, Sheffield
1911	Trans.		Merriman, Richard William, M.A. (Cantab.), 244, Victoria-park-road, South Hackney, N.E.
1897			Merson, George Fowlie, 22, Duke-street, Edinburgh
1910	Trans.		Merton, Thomas Ralph, B.Sc. (Oxon.), 25, Gilbert-street, W.
1876	Trans.	C. 1884-8, 1897-1901 V.P. 1906-9	‖Messel, Rudolph, Ph.D. (Tübingen), F.R.S., F.I.C., 147, Victoria-street, Westminster, S.W.

Date of Election.			
1915			Michie, John Livingston, 1, Duke-street, Hawick
1904			Middleditch, Bernard, B.A. (Cantab.), 7, High-street, Harrow-on-the-Hill
1906			Middleton, Alexander Edmund, Government Laboratory, Clement's Inn-passage, Strand, W.C.
1912			Middleton, Herbert, M.Sc. (Manc.), Technical College, Bradford
1888	Trans.	V.P. 1901-04	‖Miers, Sir Henry Alexander, M.A. and D.Sc. (Oxon.), Hon. D.Sc. (Sheffield), Ph.D. (Christiania), F.R.S., Birch Heys, Cromwell Range, Fallowfield, Manchester
1912			Milbourne, Robert John, Assoc.M.Inst.C.E., Midland Iron Works, Donnington, Newport, Salop.
1908			Miles, William Herbert, c/o Messrs. H. A. Fowler & Co., 167, Vauxhall-road, Liverpool
1908			Millar, Charles James, 23, James'-street, Greenhead, Glasgow
1892	Trans.		Millar, James Hill, D.Sc. (Birm.), F.I.C., Chief Chemist's Laboratory, St. James's Gate Brewery, Dublin
1891			‖Millard, Edgar James, 35-42, Charlotte-street, Great Eastern-street, E.C.
1905			Millen, John Dunlop, Mount Bischoff Mine, Waratah, Tasmania
1880	Trans.		‖Miller, Alexander Kenneth, Ph.D. (Würzburg), F.I.C., Kilvert's Buildings, Withy-grove, Manchester
1913			Miller, Arthur George Abraham, B.Sc. (Lond.), Physiological Department, Middlesex Hospital Medical School, Mortimer-street, W.
1901			Miller, Edward Holl, c/o Messrs. Robert Harper & Co., Port Melbourne, Victoria, Australia
1889	Trans.		Miller, James Bruce, A.I.C., Rubislaw Den North, Aberdeen
1887			Miller, John Albert, M.Sc. (Illinois), Ph.D. (Berlin), 44 & 45, Lewis Block, Buffalo, N.Y., U.S.A.
1911			Miller, John Watterson, M.D. (Vict. and L'pool.), B.Ch. (Vict.), D.P.H. (Cantab.), Lynwood, Cantilupe-street, Hereford
1885	Trans.		‖Miller, Norman Harry John, Ph.D. (Würzburg), F.I.C., Harpenden, Herts.
1898			Miller, William Lash, B.A. (Toronto), Ph.D. (Munich), 50, St. Alban-street, Toronto, Canada
1893	Trans.		‖Mills, Charles, A.C.G.I., F.I.C., P.O. Box 112, Kroonstad, S. Africa
1862	Trans.	C. 1868 72, 75-6, 80-4, 1903-06 V.P. 1912-15	‖Mills, Edmund James, Prof., D.Sc. (Lond.), LL.D. (Glas.), F.R.S., F.I.C., 64, Twyford-avenue, West Acton, W.
1906			Mills, Herbert Arthur, 3, Croxted-road, West Dulwich, S.E.

Date of Election.		
1911		Mills, Robert, Plantation Nitolugt W.C., Demerara, British Guiana
1898	Trans.	Mills, William Hobson, M.A. (Cantab.), Sc.D. (Tübingen), Chemical Laboratory, The University, Cambridge
1905	Trans.	Mills, William Sloan, M.A., D.Sc. and B.E. (R.U.I.), Research Department, Messrs. Levinstein, Ltd., Blackley, Manchester
1885		‖Milne, Alexander, Lieut.-Col., I.M.S., M.A., M.B. and M.Ch. (Aberd.), Morkew, Cults, Aberdeenshire
1887		Mingaye, John Charles Henderson, F.I.C., Department of Mines, Assay Branch, Sydney, N.S.W.
1898		‖Mitchell, Albert Henry, B.Sc. (Lond.), F.I.C., Borough Analyst's Laboratory, Hensleigh-road, Tiverton
1910	Trans.	Mitchell, Alec Duncan, B.Sc. (Lond.), 52, Montalt-road, Woodford Green
1916	Proc.	Mitchell, Charles Ainsworth, F.I.C., White Cottage, The Common, Amersham, Bucks.
1907	Trans.	Mitchell, Herbert Victor, c/o The British Burma Petroleum Co., Ltd., 8–12, Spark-street, Rangoon, Burma
1915		Mitchley, John William, A.M.I.Mech.E., H.M. Munitions Factory, Gretna, Carlisle
1905		‖Modi, Edalji Manekji, D.Sc. (N. Carolina), LL.D. (Tennessee), Litt.D. (Providence, Ohio), Meher-buildings, Tardeo, Bombay, India
1912		‖Modi, Pestanji Manekji, B.A. (Bombay), Meher-buildings, Tardeo, Bombay, India
1899		Mohr, Bernard, Ph.D. (Heidelberg), 69, Parliament-hill, Hampstead, N.W.
1901	Trans.	Moir, James, M.A. and D.Sc. (Aberd.), Chemical Laboratory, Mines Department, and 48, Ditton-avenue, Auckland-park, Johannesburg, S. Africa
1893		Mole, Herbert Bloome, Royal Albert Brewery, Queen's-road, Reading
1902		Molesworth, Francis Hylton, Jersey-road, Artarmon, Sydney, N.S.W.
1899		Molson, John Cavendish, M.D. (Chicago), L.R.C.P. (Lond.), The Gables, Haywards Heath
1899		Mond, Emile Schweich, 22, Hyde-park-square, W.
1892		Mond, Robert Ludwig, M.A. (Cantab.), F.R.S.E., Combe Bank, near Sevenoaks
1879		‖Mondy, Edmund Felix, Prof., A.R.S.M., Dacca, 96, Huron-road, Balham, S.W.
1903	Trans.	Monier-Williams, Gordon Wickham, M.A. (Oxon.), Ph.D. (Freiburg), F.I.C., 32, St. Leonard's-terrace, S.W.

Date of Election.			
1904			Montgomery, Jack Percival, Prof., Ph.D. (Virginia), A.M. (Clarksville), University of Alabama, University, Ala., U.S.A.
1887	Trans.	(C. 1899-1900 1905-8)	‖Moody, Gerald Tattersall, D.Sc. (Lond.), F.I.C., Lorne House, North Dulwich, S.E.
1897			Moon, Philip George Gregory, Savona, Alexandra-road, Parkstone, Dorset
1892			‖Moor, Cresacre George, M.A. (Cantab.), F.I.C., 30, Great James-street, Bedford-row, W.C.
1903			Moore, Alfred Ernest, B.A. and B.Sc. (Lond.), Rector del Colegio Nacional, Paraná, Entre Rios, Argentine, S. America
1903			Moore, Arthur, 128, Felbrigge-road, Goodmayes, Essex
1916			Moore, Arthur, B.Sc. (Manc.), 199, Windsor-road, Oldham
1905	Trans.		Moore, Charles Watson, M.Sc. (Vict.), Ph.D. (Munich), c/o Messrs. J. Crosfield & Sons, Ltd., General Laboratory, Warrington
1891			Moore, Frederick Herbert, 87 and 89, Aldgate, E.
1910			Moore, Harold, M.Sc. Tech. (Manc.), 7, Poplar-grove, Hazel Grove, Stockport
1907			Moore, John Edward Langford, Walton Cottage, Loughboro' Park, S.W.
1902			Moore, Thomas Henry, c/o Messrs. Fassett & Johnson, 5–7, Barrack-street, Sydney, N.S.W.
1904	Trans.		Moore, Tom Sidney, Prof. M.A. (Oxon.), B.Sc. (Lond.), Hillside, Egham, Surrey
1911	Trans.		Moore, Walter Roman, B.Sc. (Lond.), A.R.C.S., c/o Nobel's Explosives Co., Ltd., Pembrey Factory, Pembrey, Carmarthen
1908			Morewood, Capel Darcy, Frodingham Ironstone Mines, Scunthorpe, Lincs.
1895			Morgan, David James, M.A., M.D. and B.C. (Cantab.), D.P.H. (Lond.), The County Hall, Cardiff
1897			Morgan, Frederick Filmer de, 57, Woodberry-crescent, Muswell Hill, N.
1898	Trans.	(C. 1909-10 S. 1910-12 V.P. 1912-15)	‖Morgan, Gilbert Thomas, Prof., D.Sc. (Lond.), A.R.C.S., F.R.S., F.I.C., Finsbury Technical College, Leonard-street, E.C.
1908			Morgan, Howard Houlston, B.Sc. (Lond.), A.R.C.S., 45, Twickenham-road, Teddington
1888			‖Morgan, John James, F.I.C., Lyndhurst, Western-road, Flixton, Manchester
1900			Morgan, John Livingston Rutgers, Prof., A.M. and Ph.D. (Leipzig), B.Sc. (Rutgers College), Columbia University, New York City, U.S.A.
1912			Morgan, Sidney, Rubber Growers' Association Laboratory, Pataling, Kuala Lumpur, Federated Malay States

Date of Election.			
1880	Trans.		Moritz, Edward Ralph, Ph.D. (Göttingen), F.I.C., 45, Great Tower-street, E.C.
1879	Trans.	(C. 1887-90, 96-1900)	‖Morley, Henry Forster, M.A. and D.Sc. (Lond.), F.I.C., 5, Lyndhurst-road, South Hampstead, N.W.
1909			Morley, William Norton, B.Sc. (Lond.), 100, Burnt Ash-hill, Lee, S.E.
1912	Trans.		Morrell, George Francis, Ph.D. (Kiel), B.Sc. (Lond.), F.I.C., Sir John Cass Technical Institute, Jewry-street, Aldgate, E.C.
1895	Trans.		‖Morrell, Robert Selby, M.A. (Cantab.), Ph.D. (Würzburg), c/o Messrs. Mander Bros., Wolverhampton; and Tor Lodge, Tettenhall Wood, Wolverhampton
1890			Morris, Arthur Higgs, 152, Chorley New-road, Bolton
1900			Morris, Edgar Ford, M.A. (Oxon.), Holly Bank, Roby, Huyton, Liverpool
1905			Morris, Eric Haydn, 2, Rua da Charidade, Pajussára, Maceió, Brazil
1891			Morris, Joseph, Ph.D., Fern Bank, 8, Boardman-street, Eccles, Manchester
1914			Morris, Thomas, c/o Airey's Brewery, Ltd., Westwood-road, Poolstock, Wigan
1915			Morson, Thomas Dagomet, 27, Briardale-gardens, Hampstead, N.W.
1905			Mortimer, Alfred, B.A. (Oxon.), Letchworth School, Letchworth, Herts.
1896			Moss, Francis Ambrose, Greenbushes, Western Australia
1871			‖Moss, Richard Jackson, F.I.C., St. Aubyns, Ballybrack, Co. Dublin
1886			‖Moul, Frank, F.I.C., 5, Blakesley-avenue, Ealing, W.
1911			‖Moullin, Oswald Mansell, M.A. (Cantab.), 69, Wimpole-street, W.
1884			‖Moyle, Robert Edward, M.A. (Oxon.), Heightley, Chudleigh, S. Devon
1909			Müller, John, B.A. (Cape of Good Hope), Government Analytical Laboratory, Cape Town, S. Africa
1871	Trans.	C. 1890-4	‖Muir, Matthew Moncrieff Pattison, M.A. (Cantab.), St. Clements' Rectory, Norwich
1870			‖Muirhead, Alexander, D.Sc. (Lond.), F.R.S., The Lodge, Shortlands, Kent
1914			Mulla, Yusuf Ismail, Alembic Laboratory, Club-road, Mandalay, Burma
1913			Mumford, Ernest Joseph, 67, Hatherley-road, Walthamstow, N.E.
1912	Trans.		Mumford, Ernest Moore, M.Sc. (Manc.), 75, High-street, Chorlton-on-Medlock, Manchester

Date of Election.		
1907		Mummery, Charles Samuel, B.Sc. (Lond.), A.C.G.I., D.I.C., Laurel Bank, Queen's-road, Loughton, Essex
1902		Mundey, Alfred Holley, 14, Wrottesley-road, Plumstead, S.E.
1876	Trans.	‖Munro, John May Herbert, D.Sc. (Lond.), M.R.C.S. (Eng.), L.R.C.P. (Lond.), F.I.C., 12, Grosvenor-place, Bath
1888		Munroe, Charles Edward, Prof., George Washington University, Washington, D.C., U.S.A.
1900		Munton, Frederick Thomas, Craigmore, Winsford, Cheshire
1907		Murgatroyd, Louis, 1, Carlton-drive, Heaton, Bradford
1901		Murphy, Albert John, 3 and 4, Queen-square, Leeds
1913		Murphy, Paul, F.I.C., c/o Dr. Murphy, Beck Isle, Pickering
1904		Murray, Benjamin Lindley, A.M. (Columbia), B.S. (Mich.), c/o Messrs. Merck & Co., Manufacturing Chemists, Rahway, N.J., U.S.A.
1906		Murray, Thomas Jenkins, M.Sc. (Birm.), Ph.D. (Leipzig), Municipal Technical School, Wolverhampton
1890	Trans.	‖Murray, Thomas Smith, D.Sc. (Edin.), 27, Shamrock-street, Dundee
1869		‖Muspratt, Edmund Knowles, Hon. LL.D. (L'pool.), F.I.C., Seaforth Hall, near Liverpool
1873		‖Muspratt, Sidney Knowles, 9, Church-street, Flint, N. Wales
1896		Muter, Alexander Henry Mitchell, F.I.C., Laboratory, 325, Kennington-road, S.E.; and The Châtelet, Horley, Surrey
1914		Myddleton, William Whalley, M.Sc. (Belfast), 6, Cawley-street, Runcorn
1912		Myers, Ernest Meyer, 6, Lower-crescent, Harpfields, Stoke-on-Trent
1910	Trans.	Myers, James Eckersley, B.Sc. (Manc.), 7, Station-road, Cheadle Hulme, Stockport
1892	Trans.	Myers, William Shields, D.Sc. (N.J.), M.Sc. (New Brunswick), B.Sc. (Rutgers Coll.), 25, Madison-avenue, New York City, U.S.A.
1887		Nagel, David Henry, M.A. (Oxon.), Trinity College, Oxford
1916		Naidu, Bangalore Pasupulcti Balakrishna, M.B., Ch.B. (Edin.), M.H., D.P.H., & D.T.M. (L'pool), 83, Indian Stationary Hospital, I.E. Force "D," c/o Presidency Post Master, Bombay
1913		Naik, Kunerji Gosai, Prof., M.A., and B.Sc. (Bombay), Krishnath College, Berhampore, District Murshidabad, Bengal, India
1910		Nair, Valliyil Govindan, B.A. (Madras), M.Sc. Tech. (Manc.), Société Cotonniére du Tonkin, Nam Dink, Tonkin, French Indo-China

Date of Election.		
1903		Nairne, Urban Orlando Scotchburn, 1, Eglantine-road, Wandsworth, S.W.
1874		‖Napier, Arthur Sampson, Prof., B.Sc. (Oxon.), c/o Herren Mayer and Müller, 2, Prinz Louis Ferdinandstrasse, Berlin
1893		Napier, John Watson, Corporation Gas Works, Alloa
1915		Napier, Oswald James Walter, B.A. (Cantab.), 6, Victoria-street, Musselborough, Dunedin, New Zealand
1909		Napier, Thomas, c/o The Cassel Cyanide Co., Ltd., Maryhill, Glasgow
1900	Trans.	Napper, Sidney Scrivener, A.C.G.I., A.I.C., c/o Messrs. S. Courtauld and Co., Ltd., Foleshill-road, Coventry
1910		Narbeth, Benjamin Mason, B.Sc. (Wales and Cape), The Technical College, Durban, Natal, S. Africa
1915		Nash, Elton Arthur, c/o Colonial Iron Co., Riddlesburg, Pa., U.S.A.
1898		Nash, Leonard Myddelton, F.I.C., 3, Princess-road, Finsbury Park, N.
1912		Natrajan, Tanjore S., Prof., 315, Linghi Chetty-street, Madras E., India
1912	Trans.	Naunton, William Johnson Smith, M.A. (Cantab.), B.Sc. (Lond.), Dip. Chem. (Munich), A.I.C., The Thoroughfare, Woodbridge
1900		Naylor, Ernest Brooks, M.Sc. (Vict.), F.I.C., Eversleigh, Gathurst, Wigan
1913	Trans.	Naylor, Jonathan Harold, M.Sc. (Manc.), F.I.C., Braemore, Flinn-lane, Frodsham, Warrington.
1891		Naylor, William, 3, Garstang-road, Fulwood-park, Preston
1878	Trans.	Naylor, William Arthur Harrison, F.I.C., The British Drug Houses, Ltd., 22–30, Graham-street, City-road, N.
1910		Neal, George William, B.Sc. (Lond.), Shalom, Manor-way, Beckenham
1908		Neech, Herbert Richard, Doddington-road, Swallowbeck, Lincoln
1910		Needs, Francis Edwin, 7, Effingham-road, St. Andrew's-Park, Bristol
1898		Neilson, Alexander MacGillivray, Umbilo Post Office, viâ Durban, Natal, S. Africa
1912		Neilson, Richard Gillies, c/o Anglo-Persian Oil Co., Mohammerah, Persia, viâ Bombay and Persian Gulf
1908	Trans.	Neogi, Punchānan, Prof., M.A. (Calcutta), Rajshahi College, Rajshahi, Bengal, India
1901		Neumann, Edgar David Maurice, M.A. (Oxon.), Ph.D. (Göttingen), A.I.C., 7 & 8, Idol-lane, E.C.
1871	Trans.	‖Nevill, Edmund Neville, F.R.S., F.I.C., 59, Enys-road, Eastbourne

Date of Election.		
1905	Trans.	Neville, Henry Allen Dugdale, B.A. (Cantab.), B.Sc. (Lond.), F.I.C., Elms Hall, Colne Engaine, Earls Colne, Essex
1892		‖Newall, John Fenton, St. James's-buildings, Oxford-street, Manchester
1885		‖Newbolt, Francis George, M.A. (Oxon.), Balliol College, Laboratory, Oxford
1914		Newland, Alfred Edgar, Prof., The Government University, Peking, China
1891		‖Newlands, William Peter Reina, 10, Cricklade-avenue, Streatham Hill, S.W.
1912		Newman, Leslie Frank, M.A. (Cantab.), Downing College, Cambridge
1894	Trans.	Newth, George Samuel, F.I.C., 7, Shakespeare-terrace, Folkestone
1914		Newton, Arthur Ulysses, B.Sc. (Lond.), 37, Netherhall-gardens, Hampstead, N.W.
1895		Newton, Charles Butterworth, M.Inst.C.E., Town Hall, Hull
1911		Newton, Leonard Owen, 41, Bennett-park, Blackheath, S.E.
1899	Trans.	Nicholls, William Walter Scott, B.Sc. (Lond.), c/o Mrs. Tyrrell, 8, Foxwell-street, Brockley, S.E.
1913		Nichols, John Allen, Stanley Mount, New Mills, Stockport
1914		Nichols, Raymond William, Central Experimental Farm, Ottawa, Canada
1912		Nichols, William Moore, Edgerton, Park-avenue, Castleford
1870	Trans.	‖Nicholson, Edward, Brigade Surgeon, Lieut.-Col., M.R.C.S. (Eng.), L.S.A. (Lond.), D.P.H. (Cantab.), F.I.C., 111, Avenue de Neuilly, Neuilly-sur-Seine, Paris, France
1910		Nicholson, Philip Brady, West Melton, Rotherham
1889		Nickels, Wallace Christopher, 41, Cheapside, E.C.
1883	Trans.	Nicol, William Walker James, M.A. and D.Sc. (Edin.), F.I.C., 15, Blacket-place, Edinburgh
1912	Trans.	Nierenstein, Maximilian, Ph.D. (Berne), 30, Cavendish-road, Henleaze, Bristol
1900		Nightingale, Thomas Marginson, B.Sc. (Vict.), 117, High-street, Bolton
1898		Nightscales, Thomas Arthur, 642, Holderness-road, Hull
1913	Trans.	Nolan, Thomas Joseph, D.Sc. (N.U.I.), M.Sc. (Dub.), 10, Arran-place, Ardrossan
1903	Trans.	Norman, George Marshall, B.Sc. (Lond.), A.R.C.S., F.I.C., 135, Walmersley-road, Bury
1889		Norman, John Thomas, 23, Leadenhall-street, E.C.
1908	Trans.	Normand, Alexander Robert, M.A. and B.Sc. (Edin.), Wilson College, Bombay, India
1892		Norris, Charles James, 31, Airedale-avenue, Chiswick, W.

Date of Election.			
1909	Trans.		Norris, Roland Victor, D.Sc. (Lond.), M.Sc. (Manc.), F.I.C., c/o Mrs. R. V. Norris, Lister Institute, Chelsea Gardens, S.W.
1897	Trans.		North, Barker, 33, Ashgrove, Great Horton-road, Bradford
1892			Northing, John, The Murrough, Wicklow
1878			‖Norton, Thomas Herbert, Prof., Ph.D. (Heidelberg), D.Sc. (Hamilton), c/o The American Consulate, Theaterstrasse, 14, Chemnitz, Saxony, Germany
1901			Nunn, Arthur William, 57, Crouch-street, Colchester
1907	Trans.		Nuttall, Walter Harold, F.I.C., 75, Mildred-avenue, Watford
1904			Oakden, William Edward, 11, Lonsdale-road, Barnes, S.W.
1899			Oakfield, William Frederick, 18, Maryon-road, Charlton, S.E.
1910			Oakley, Robert O'Field, c/o The Patent Office, 25, Southampton-buildings, Chancery-lane, W.C.
1893	Trans.		Oates, William Henry, Townhead, Dore, Sheffield
1907			Oberländer, Otto, Ph.D. (Heidelberg), 29, Queen-street, E.C.
1903			O'Brien, Frederick, M.Sc. (L'pool.), Pineleigh, Burnett-road, Saltford, Bristol
1890			Oddy, Robert Walter, F.I.C., Waterhouse, Toad-lane, Rochdale
1873			‖Odling, Walter, F.I.C., c/o Messrs. Bass and Co., Burton-on-Trent
1848	Trans.	S. 1856-69 V.P. 1869-73 P. 1873-5	Odling, William, Prof., M.A. (Oxon.), M.B. and F.R.C.P. (Lond.), Hon. Ph.D. (Leyden), F.R.S., F.I.C., 15, Norham-gardens, Oxford
1914			Odlum, William Julian, B.A. (Dub.), Ardmore, Bray, Co. Wicklow
1916	Trans.		Oesch, Joseph Bernhard, Ph.D. (Zürich), The University, Leeds
1905			‖O'Farrelly, Alfons, M.A. (R.U.I.), 26, Highfield-road, Rathgar, Dublin
1912			Ogilvie, James Pettigrew, 2, St. Dunstan's-hill, E.C.
1908			‖Oke, Alfred William, B.A. and LL.M. (Cantab.), 32, Denmark-villas, Hove, Sussex
1909			Okell, Frederick Leigh, F.I.C., c/o Straits Trading Co., Ltd., Singapore, Straits Settlements
1908			Okell, Stanley Allen Warrington, c/o The West Virginia Pulp and Paper Co., 521, W. 23rd-street, New York City, U.S.A.
1901			Oldershaw, William, J.P., The Firs, Kimberley, Nottingham
1916			Oldham, John Walter Hyde, B.A. (Cantab.), Trinity College, Cambridge
1914			Oldroyd, Rowland Ernest, 90, Park-road, Rochdale
1913			Oliver, Ralph Richard, c/o The Southern Fibre Co., Portsmouth, Va., U.S.A.
1915			Ollé, Archibald Durrant, 28, Charlotte-street, Ashfield, N.S.W.
1889			‖O'Mahony, Daniel John, Municipal-buildings, Cork
1889			‖O'Mara, James, B.A. (R.U.I.), Cork-Street, Dublin

Date of Election.			
1901			Oram, Frank, Market-place, Romsey
1912	Trans.		Orange, Lionel, B.Sc. (Lond.), A.I.C., 148, Barkworth-road, N. Camberwell, S.E.
1890	Trans.		Ormandy, William Reginald, D.Sc., Imperial House, Kingsway, W.C.
1872			‖Ormerod, Joseph Arderne, M.D. (Oxon.), M.R.C.S. (Eng.), F.R.C.P. (Lond.), The Library, St. Bartholomew's Hospital, E.C.
1887			‖Ormiston, Archibald Reid, Braeholm, Helensburgh; and 213, St. Vincent-street, Glasgow
1881			Orr, John Bryson, Crossacres, Much Woolton, Liverpool
1897	Trans.	C. 1913-	‖Orton, Kennedy Joseph Previté, Prof., M.A. (Cantab.), Ph.D. (Heidelberg), F.I.C., Wylfa, and University College of North Wales, Bangor
1881	Trans.		O'Shea, Lucius Trant, Prof., M.Sc. (Sheffield), B.Sc. (Lond.), The University, Sheffield
1887			Ostersetzer, Julius, F.I.C., c/o Messrs. W. and H. M. Goulding, Manure Manufacturers, North Wall, Dublin
1883	Trans.		O'Sullivan, James, F.I.C., High Bank, Burton-on-Trent
1887			‖O'Sullivan, Patrick Thomas, M.D. and B.Ch. (R.U.I.), 20, South Mall, Cork
1891			Ough, Lewis, Fernleigh, St. James's-road, Leicester
1915			Outram, Reginald Robert, Trinity Grammar School, Kew, Victoria, N.S.W., Australia
1888			Overbeck, Otto Christoph Joseph Gerhard Ludwig, Chantry House, Great Grimsby
1887			‖Overend, Frederick Lawrence, B.A. (Oxon.), Lyndhurst, Leigh-road, Walsall
1916			Owen, Frederick, 16, Brooke-street, Bradford, Manchester
1911			Owen, Idris Larkby, M.Sc. (L'pool), The Hollies, Robin Hood-lane, Hall Green, Birmingham
1911	Trans.		Page, Harold James, B.Sc. (Lond.), Elmdene, Derry Downs, St. Mary Cray, Kent
1916			Page, Hubert Ernest, H.M. Factory, Queen's Ferry, Chester
1913			Paget, Ferrand, 73, Stanhope-avenue, Church End, Finchley, N.
1909			Painter, Frederick Hubert, B.Sc. (Lond.), 29, Talbot-road, Winton, Bournemouth
1884			‖Pallister, John William, B.Sc. (Lond.), 107, Waverley-road, Bradford
1910			Palmer, Gilbert, B.Sc. (Lond.), Burwell, Prospect-road, Ash Vale, Aldershot

Date of Election.		
1899		Palmer, Thomas Henry, c/o Broken Hill Junction North Silver Mining Co., P.O. Box 98, Broken Hill, N.S.W.
1912	Trans.	Paniker, Ramni, M.A. (Madras), M.Sc. (Leeds), Consejo de Ciento, 288, Barcelona, Spain
1902		Panisset, Sydney Glyde Stephen, Markgate House, Jennings-road, St. Albans
1899	Trans.	Panting, Laurence Christopher, M.A., M.D. and B.Ch. (Oxon.), F.R.C.S. (Eng.), M.R.C.P. (Lond.), Gwendroc, Truro
1915	Trans.	Parker, Albert, D.Sc. (Birm.), M.Sc. (Manc.), The University, Birmingham
1898		Parker, Alfred James, 1, Bulwer-street, Herne Bay, Auckland, New Zealand
1913		Parker, Jonathan, 144, Queen-street, Whitehaven
1882		Parker, Joseph Richard, Millook, Branscombe-gardens, Winchmore Hill, N.
1894	Trans.	Parker, Matthew Archibald, Prof., B.Sc. (Glas.), University of Manitoba, Winnipeg, Canada
1916	Trans.	Parker, Reginald George, B.Sc. (Lond.), A.C.G.I., 63, Gondar-gardens, Hampstead, N.W.
1882		‖Parker, Robert Henry, Ravenscar, Orchard-drive, Blackheath, S.E.
1901		Parkes, Albert Edward, F.I.C., Chemical Laboratory, 43, Whitehorse-street, Stepney, E.
1912	Trans.	Parkes, John Wilfrid, Merton House, Arklow, Co. Wicklow
1911		Parkes, Thomas Peers, B.Sc. (Lond.), 114, Wickham-road, Brockley, S.E.
1906		‖Parkin, John, M.A. (Cantab.), The Gill, Brayton, Aspatria, Cumberland
1865	Trans.	‖Parkinson, James, Queen's-chambers, Pirie-street, Adelaide, S. Australia
1893		‖Parrish, Samuel, B.Sc. (Lond.), 80, Grange-avenue, Chapeltown-road, Leeds
1892		Parry, Ernest John, B.Sc. (Lond.), F.I.C., Thanet House, 56A, Great Dover-street, S.E.
1903	Trans.	Parry, William, B.Sc. (Lond.), Glenamour, Waterloo-park, Liverpool
1911		Partington, Edward, Oakdene, Sedgley-park, Manchester
1914	Trans.	Partington, James Riddick, B.Sc. (Manc.), School-lane, Lostock Gralam, Northwich
1894	Trans.	Paterson, David, F.R.S.E., Lea Bank, Rosslyn, Midlothian
1910		Paterson, John Hamilton, D.Sc. (Dundee), 40, Blandford-street, Sunderland
1912		Patterson, John William, 23, Ferndene-road, Herne Hill, S.E.
1896		Patterson, Joseph William, 56, Grange-road, West Hartlepool

Date of Election.			
1904	Trans.		Patterson, Thomas Stewart, D.Sc. (Lond. and Glas.), Ph.D. (Heidelberg), Chemical Department, The University, Glasgow
1913			Pattison, John Thomas, 45, Hudson-road, Southsea
1868	Trans.		‖Paul, Benjamin Horatio, Ph.D. (Giessen), Parkside, Kingston Vale, Putney, S.W.
1911			Paul, Felix Gabriel, 35, 39th-street, Rangoon, Burma
1885	Trans.		Paul, Lewis Gordon, Ph.D. (Tübingen), F.I.C., Market Hall-chambers, King-street, Huddersfield
1896			Payne, Arthur, c/o Messrs. Mawson and Swan, Moseley-street, Newcastle-on-Tyne
1893			Payne, George Frederick, M.D. (Atlanta), 60, Armstrong-street, Atlanta, Georgia, U.S.A.
1915			Peachey, Frank, B.Sc. (Lond.), Evesden, The Forest, Snaresbrook, N.E.
1899	Trans.		Peachey, Stanley John, M.Sc. (Manc.), School of Technology, Sackville-street, Manchester
1901			Peacock, Arthur, B.Sc. (Vict.), The Brebner Schools, Bloemfontein, S. Africa
1911	Trans.		Peacock, David Henry, B.A. (Cantab.), B.Sc. (Lond.), A.I.C., 25, Forrest-avenue, Marsh, Huddersfield
1874			Pearce, Sir William, M.P., Chemical Works, Bow Common, E.
1915			Pearson, Archibald Ramsden, B.Sc. (Lond.), A.R.C.S., A.I.C., Government Laboratory, Clement's Inn-passage, Strand, W.C.
1908			Pearson, George Edward, c/o Messrs. Burroughs, Wellcome & Co., Snow Hill Buildings, E.C.
1912			Pearson, George Ernest, 240, Goswell-road, E.C.
1908			Pearson, John William, B.A. (Cantab.), 35, Orford-road, Warrington
1894	Trans.		Pearson, William Henry, Suffolk House, Cannon-street, E.C.
1902			Peck, John Wicliffe, The Hospital for Sick Children, Great Ormond-street, W.C.
1911	Trans.		Peddle, Cyril James, M.Sc. (Sheffield), Wood View House, Silkstone Common, Barnsley
1894			Peden, John, 13, Manor-road, Bellahouston, Glasgow
1870	Trans.	{ V.P. 1907-10 }	‖Pedler, Sir Alexander, Prof., C.I.E., F.R.S., F.I.C., 28, Stanhope-gardens, Queen's Gate, S.W.
1904			Pell, Alfred, 44, Cumballa-hill, Bombay, India
1886	Proc.		Pendlebury, William Henry, M.A. (Oxon.), Broadlands, Canonbury, Shrewsbury
1916			Penfold, Arthur Ramon, Langlo, 34, Alt-street, Ashfield, Sydney, N.S.W.
1870			Penney, Mulgrave Daniel, 11, High-street, Hull
1910			Pennington, Alfred John, Oakley, Fallowfield, Manchester

Date of Election.			
1895			Pennington, William Henry, Sykeroyd, Holmefield-avenue, Cleveleys, Blackpool
1886			Pentecost, Stephen James, Lenton Works, Nottingham
1884	Trans.	C. 1906-10	Perkin, Arthur George, Prof., F.R.S., F.I.C., The University, and Grosvenor Lodge, Grosvenor-road, Leeds
1891	Trans.		‖Perkin, Frederick Mollwo, Ph.D. (Würzburg), F.I.C., 199, Piccadilly, W.
1884	Trans.	C. 1891-5 V.P. 1906-9 P. 1913-15	†Perkin, William Henry, Prof., Ph.D. (Würzburg), Hon. Sc.D. (Cantab.), Hon. LL.D. (Edin. and St. Andrews), F.R.S., F.I.C., 5, Charlbury-road, Oxford
1906	Trans.		Perkins, William Hughes, B.Sc. (Manc.), The University, Leeds
1890	Trans.		‖Perman, Edgar Philip, D.Sc. (Lond.), University College, Cardiff
1905			Perrott, Bert, Bryn Clydach, Neath Abbey, Neath
1908			Perry, Frank, 103, Dudley-road, Tipton
1900			Pettigrew, Robert, 44, Mosley-street, Manchester
1902	Trans.		Phelps, John, M.A. (Oxon.), The Royal Mint, E. ; and Newcroft, Egmont-road, Sutton, Surrey
1881			Philip, Arnold, B.Sc. (Lond.), A.R.S.M., F.I.C., Chemical Laboratory, H.M. Dockyard, Portsmouth
1897	Trans.	C. 1910-13 S. 1913-	Philip, James Charles, Prof., M.A. and D.Sc. (Aberd.), Ph.D. (Göttingen), Imperial College of Science and Technology, S. Kensington, S.W., and 17, Fairfax-road, Bedford Park, W.
1904			Phillips, George Frederick Tyler, M.Sc. (Lond.), University College, Southampton
1897	Trans.		Phillips, Harry Edward William, M.A. and B.Sc. (Oxon.), Church House, Summertown, Oxford
1882			Phillips, Henry Harcourt, Laboratory, Court Chambers, Mawdsley-street, Bolton
1902	Trans.		‖Phillips, Percy Philip, Prof., Ph.D. (Göttingen), F.I.C., Thomason Engineering College, Rurki, U.P., India
1908			Phillips, Thomas Richard, 5, Enmore-road, Putney, S.W.
1905			Phipson, Percy Barker, c/o Messrs. J. Staples and Co., Ltd., Wellington, New Zealand
1914			Pick, William Henry, B.Sc. (Lond.), 141, Mare-street, Hackney, N.E.
1909	Trans.	C. 1916-	Pickard, Joseph Allen, B.Sc. (Lond.), A.R.C.S., A.I.C., 186-188, Walmer-road, Notting Hill, W.
1897	Trans.		‖Pickard, Robert Howson, D.Sc. (Lond.), Ph.D. (Munich), B.Sc. (Birm.), F.I.C., Municipal Technical School, Blackburn
1891			Pickering, Michael Samuel, B.Sc. (Lond.), 38, Price-street, Burslem

† Longstaff Medallist, 1900.

Date of Election			
1878	Trans.	(C. 1886-7, 89-93, 1901-04.)	‖Pickering, Spencer Percival Umfreville, M.A. (Oxon.), F.R.S., F.I.C., Harpenden, Herts.
1906	Trans.		Pickles, Samuel Shrowder, D.Sc. (Vict.), c/o Messrs. George Spencer, Moulton & Co., Ltd., Bradford-on-Avon
1913			Pickworth, Frederick Alfred, B.Sc. (Lond.), A.I.C., 70, Highfield-road, Dartford
1890	Trans.		‖Picton, Harold, B.Sc. (Lond.), The Thatch, Ugley-green, Bishop's Stortford
1909	Trans.		Picton, Norman, B.Sc. (Wales), Ph.D. (Leipzig), 31, South Beach-avenue, Ardrossan
1916			Pierson, George Humphrey, 6, Station-road, New Barnet, BO., Herts.
1874	Trans.		‖Pike, William Herbert, Prof., Ph.D. (Göttingen), Sandhills, Salcombe, Devon
1883			‖Pilley, John J., Ph.D., 167, Camberwell-grove, S.E.
1896			Pilley, Thomas William, 33, Grove-hill-road, Denmark Hill, S.E.
1889			Ping, William, 14, Selsdon-road, Wanstead, N.E.
1908			Pingriff, George Neville, B.A. (Cantab.), University College School, Hampstead, N.W.
1889			‖Pingstone, George Arthur, P.O. Box 445, Bulawayo, S. Africa
1904			Pinkerton, David John, Dalzell Steel and Iron Works, Motherwell
1908			Pinnock, Douglas Robert, A.C.G.I., c/o The Nucoa Butter Co., 4th-street and Avenue A, Bayonne, N.J., U.S.A.
1881			Pisani, Orestes Victoriano, 188, Cavendish-road, Clapham Park, S.W.
1903	Trans.		Pitt, Arthur Ernest, Broad View, Chigwell-road, South Woodford, N.E.
1903			Pitt, Harold Russell, 240, Burrage-road, Plumstead, S.E.
1911			Pitt, Leonard Ison, B.Sc. (Lond.), The School, Stamford
1882			‖Pitt, Theophilus, Highleigh, Sidlesham, Chichester
1899			Pittuck, Frederick Williams, 19, Stratford-grove, Heaton, Newcastle-on-Tyne
1915			Piutti, Arnaldo, Prof., 106, Rettifilo, Naples, Italy
1899			Pizey, James Henry, A.R.C.S., F.I.C., 38, Lewisham-road, Dartmouth Park, N.W.
1893			Platt, Charles, M.D., Ph.D., Hamilton-court, 39th and Chestnut-streets, Philadelphia, U.S.A.
1911			Plews, Frank Henry, 28, Gellatly-road, St. Catherine's Park, S.E.
1899	Trans.	C. 1914-	‖Plimmer, Robert Henry Aders, D.Sc. (Lond.), 11, Ranulf-road, Hampstead, N.W. (P.O. Cricklewood)
1907			Pochin, Harold, M.A. (Cantab.), Municipal Technical School, Sutton Coldfield, Birmingham

Date of Election.			
1915			Polack, Wilfrid Gustav, M.Sc. (L'pool), Beacon Mount, Highlands-road, Runcorn
1898	Trans.		Pollard, William, M.A. (Cantab.), D.Sc. (Tübingen), F.I.C., Oakfield, Hitchin
1903			‖Pollard, William Branch, B.A. (Cantab.), Laboratory-buildings, Public-works-gardens, Cairo, Egypt
1902			Pollitt, George Paton, B.Sc. (Vict.), Ph.D. (Bâle), 4, Whitehall-court, S.W.
1901			Pollitt, James Charles Tomlin, Sharrow, The Lickey, Bromsgrove
1914	Trans.		Pollock, Ernest Ferguson, Ph.D. (Jena), F.I.C., Kirkland, Bonhill, Dumbartonshire
1903			Pond, George Gilbert, Prof., M.A. and Ph.D. (Amherst), State College, Pennsylvania, U.S.A.
1890			Pond, James Alexander, Auckland, New Zealand
1909	Trans.		Pope, Frank George, D.Sc. (Lond.), 17, Herbert-road, Wimbledon, S.W.
1912			Pope, Rupert William, B.Sc. (Lond.), A.I.C., 10, Malpas-road, Brockley, S.E.
1898	Trans.		Pope, Thomas Henry, B.Sc. (Birm.), A.C.G.I., F.I.C., Brewing School, The University, Birmingham
1891	Trans.	(C. 1900-2) (V.P. 1911-14)	†‖Pope, William Jackson, Prof., Hon. M.A. (Cantab.), Hon. D.Sc. (Manc.), Hon. LL.D. (St. Andrews), F.R.S., F.C.G.I., F.I.C., Chemical Laboratories, The University, and Holmesdale, Brooklands-avenue, Cambridge
1906			Porritt, Benjamin Dawson, B.Sc. (Lond.), F.I.C., 64, Strathearn-road, Edinburgh
1915	Trans.		Porter, James Walker, A.R.C.S.I., A.I.C., H.M.'s Factory, Queen's Ferry, Chester
1884	Proc.		‖Porter, Thomas Cunningham, M.A. and D.Sc. (Oxon.), Upton-park, Slough ; and Eton College, Windsor
1904			‖Porter, Thomas Linton Daniel, B.A., and B.Sc. (Lond.), A.K.C., 162, Coventry-road, Ilford, E.
1915			Potter, Alfred, 16, Nelson-street, Lower Broughton, Manchester
1883			Potter, Charles Edward, c/o Messrs. Tate and Sons, Love-lane Sugar Refinery, Liverpool
1912	Trans.		Potter, Charles Etty, B.Sc. (Manc.), 9, Church-view, Church-lane, Heckmondwike, Yorks.
1913			Potter, Francis Martin, B.Sc. (Lond.), A.R.C.S., F.I.C., H.M. Factory, Penrhyndeudraeth, Merioneth.
1912			Potter, Howard Vincent, B.Sc. (Lond.), A.I.C., c/o Damard Lacquer Co., Ltd., 98, Bradford-street, Birmingham
1896			Potts, Henry William, Hawkesbury Agricultural College, Richmond, N.S.W.

† Longstaff Medallist, 1903.

Date of Election.			
1913			Pougnet, Julien Pierre Frederic, c/o The Umkomaas Central Sugar Mill, Umkomaas, Natal, S. Africa
1884			‖Power, Francis Reginald, The Royal Mint, Melbourne, Australia
1896	Trans.		Power, Frederick Belding, Ph.D. (Strassburg), Hon. LL.D. (Wisconsin), Bureau of Chemistry, U.S. Department of Agriculture, Washington, D.C., U.S.A.
1908			Power, George O'Brien, Assistant Opium Agent, Basti, B.N.W. Railway, India
1913			Pracy, Henry Edward Findlater, 25, Grosvenor-park, Camberwell, S.E.
1910			Prasad, Hari, Prof., B.A. (Punjab), B.Sc. (Manc.), Government College, Ajmer, India
1914	Trans		Pratt, Walter Ryley, B.Sc. (Lond.), F.I.C., 17, Bloomsbury-square, W.C.
1904	Trans.		Prentice, Bertram, Ph.D. (Munich), D.Sc. (Edin.), Royal Technical Institute, Salford
1910			Preston, Knowles, 35, Auckland-road, Ilford
1882			‖Price, Arthur Faraday, 503, Market-street, San Francisco, Cal., U.S.A.
1899			Price, Robert Coleman, Prof., The Miller School, P.O., Albemarle Co., Va., U.S.A.
1901	Trans.		Price, Thomas Slater, D.Sc. (Lond. and Birm.), Ph.D. (Leipzig), F.I.C., 70, Erlanger-road, New Cross, S.E.
1889			‖Priestley, Charles William, B.Sc. (Lond.), A.R.C.S., Richmond Lodge, Torquay
1916			Probert, Maurice Ernest, Trevine, Hadley-road, New Barnet, BO., Herts.
1871	Trans.		‖Procter, Henry Richardson, Emeritus Prof., Hon. D.Sc. (Leeds), F.I.C., The Grange, Ilkley, and The University, Leeds
1889	Trans.		Proctor, Charles, F.I.C., 118, Grosvenor-road, Westminster, S.W.
1909			Proud, Charles, 12, Chancellor-road, Southend-on-Sea
1882			‖Pullar, Rufus Daniell, Brahan, Perth
1902			Puntan, Herbert Harding Cruikshank, Borough Analyst's Office, London-chambers, Durban, Natal, S. Africa
1875	Trans.	C 1888-92 V.P.1899-1902	Purdie, Thomas, Emeritus Prof., Ph.D. (Würzburg), Hon. LL.D. (Aberd.), B.Sc. (Lond.), A.R.S.M., F.R.S., F.I.C., The University, St. Andrews
1901	Trans.		Purvis, John Edward, M.A. (Cantab.), A.R.C.S.I., F.I.C., University Chemical Laboratory, Cambridge
1886			Pyke, Lazarus Simon Magnus, Assoc.M.Inst.C.E., M.Inst.E.E., 10, Westbourne-terrace, Hyde Park, W.
1905	Trans.	C. 1916–	Pyman, Frank Lee, D.Sc. (Vict.), Ph.D. (Bâle), Sedgley, Selborne-road, Sidcup, Kent

Date of Election.		
1905		Quant, Ernest, 2, Park-crescent, Torquay
1868		Quibell, Oliver, Shalem Lodge, Newark
1894		Quinn, Gerald Grattan, A.R.C.S., Rochdale Technical School, Rochdale
1913	Trans.	Rae, William Norman, Prof., B.A. (Cantab.), Technical Schools, Colombo, Ceylon
1914		Rai, Hashmat, B.A. and M.Sc. (Punjab), Chemical Buildings, Government College, Lahore, India
1912		Raitt, William, Kutta P.O., Coorg, India
1912	Trans.	Rakshit, Jitendra Nath, Government Opium Factory, Ghazipur, India
1902		Ralphs, Edwin, Education Department, Hong Kong
1892	Trans.	‖Ramage, Hugh, M.A. (Cantab.), A.R.C.S.I., F.I.C., Ridgemont, Carrow-hill, Norwich
1916		Ramsay, William George, B.Sc. (Lond.), Beechcroft, Hazlemere, High Wycombe
1910		Ramsden, Frederick Valentine, The Royal Mint, Melbourne, Australia
1885		Ranken, Charles, Stockton-road, Sunderland
1889		Ransom, Francis, The Chilterns, Hitchin
1910		Ransome, Alfred Oswald, Emlin Hall, Tarver, Coniston, Lancs.
1911	Trans.	Raper, Henry Stanley, M.Sc. (Vict.), A.I.C., Medical School, The University, Leeds
1914		Ratcliffe, Henry, Upper Moor Villa, Pudsey, Leeds
1914		Ratcliffe, Henry Cecil, 24A, Woodside-road, Bowes Park, N.
1898		Ratcliffe, Walter, 21, Mawdsley-street, Bolton
1905	Trans.	Ratcliffe, William Henry, B.Sc. (Lond.), Tenison's School, Leicester-square, W.C.
1915		Rau, Kodlapur Bhima, B.A. (Madras), Sankarapuram, Bangalore, Mysore, India
1910		Rau, Malur Srinivasa, M.A., M.D. and B.Sc. (Edin.), D.P.H. (Cantab.), The Chemical Laboratory and Bacteriological Institute, Bangalore, Mysore, S. India
1880	Trans.	‖Rawson, Christopher, F.I.C., 22, Cumberland-street, Manchester
1908		Ray, Haradhan, M.A. (Calcutta), c/o Messrs. Ray Bros., 51-1, College-street, Calcutta, India
1902	Trans.	Rây, Prafulla Chandra, Prof., C.I.E., D.Sc. (Edin.), Hon. D.Sc. (Dun.), Hon. Ph.D. (Calcutta), Presidency College, Calcutta
1916		Raymond, Leonard William, B.A. and B.Sc. (Lond.), A.R.C.S., 68, Charlwood-road, Putney, S.W.
1911		Raymond, Percy James, 11, Wightman-road, Harringay, N.

Date of Election.			
1912			Rayner, Edgar Alexander, B.Sc. (Lond.), A.I.C., c/o Messrs. Johnson & Sons, 23, Cross-street, Finsbury, E.C.
1889	Trans.		‖Read, Arthur Avery, Prof., D.Met. (Sheffield), F.I.C., University College, Newport-road, Cardiff
1895			Read, Edwin James, B.A. (Cantab.), F.I.C., c/o The Pretoria Portland Cement Co., Ltd., P.O. Box 405, Pretoria, S. Africa
1899	Trans.		‖Read, Harold McLean, The Briers, North Park-avenue, Roundhay, Leeds
1916	Trans.		Read, John, Prof., M.A. (Cantab.), Ph.D. (Zurich), B.Sc. (Lond.), The University, Sydney, N.S.W.
1900			Readman, James Fraser, 24, Hamilton-drive, Glasgow, W.
1910			Reddie, John Alexander, Sewage Disposal Works, Halifax
1890			Redding, Richard James, 29, Isla-road, Plumstead, S.E.
1906	Proc.		Redgrove, Herbert Stanley, B.Sc. (Lond.), 191, Camden-road, N.W.
1892			Redman, Henry Ramsden, Oaklands, Barnsole-road, Gillingham, Kent
1866		(C. 1891-2) (1910-14)	Redwood, Sir Boverton, Bart., Hon. D.Sc. (Ohio), F.R.S.E., F.I.C., 4, Bishopsgate-street-within, E.C.
1889			Redwood, Robert, 4, Bishopsgate-street-within, E.C.
1886	Trans.		Rée, Alfred, Ph.D. (Berne), 15, Mauldeth-road, Withington, Manchester
1882	Proc.		Reed, Lester, F.I.C., Hyrsthof, 19, South-park-hill-road, South Croydon
1910	Trans.		Reed, Walter William, M.Sc. (Wales), F.I.C., Technical Institute, Norwich
1910			Rees, John James Beaumont, B.Sc. (Lond.), King Edward VII. Hospital, Johannesburg, S. Africa
1914	Proc.		Reeve, Walter William, B.Sc. (Lond.), 6, Gowlett-road, E. Dulwich, S.E.
1909			Regan, Colston James, B.Sc. (Lond.), 14, Penerley-road, Catford, S.E.
1880			‖Regester, William, 13, Corfton-road, Ealing, W.
1897			Reid, Alexander Ferguson, 58, George-street, Mile End, Glasgow
1893			Reid, Thomas Anderson, 3, Edward-place, Annan
1881			‖Reid, Walter Francis, F.I.C., Fieldside, Addlestone, Surrey
1911	Trans.		Reilly, Joseph, M.A. and M.Sc. (N.U.I.), A.R.C.S.I., Chemical Laboratory, Royal Naval Cordite Factory, Halton Heath, Wareham, Dorset
1910			Rele, Gangaram Rajendrarao, c/o Messrs. Morargee, Goculdass Mills, Ltd., Bombay, India
1912			Remers, Martin, L.R.C.P. and L.R.C.S. (Edin.), 761, Rochdale-road, Manchester

Date of Election.			
1907	Trans.		Remfry, Frederic George Percy, B.A. (Cantab.), D.Sc. (Geneva), c/o Hall Motor Fuel, Ltd., Angel-road, Edmonton, N.
1897			Remington, John Stewart, Aynsome, Grange-over-Sands, Carnforth
1886			Remington, Joseph Price, Prof., 1832, Pine-street, Philadelphia, U.S.A.
1908			Rennie, Alexander, P.O. Box 703, Johannesburg, Transvaal, S. Africa
1879	Trans.		Rennie, Edward Henry, Prof., D.Sc. (Lond.), F.I.C., The University, Adelaide, S. Australia
1912			Rennie, John, c/o Messrs. W. B. Cartwright, Ltd., Lakeside Works, Rawdon, Leeds
1898	Proc.		Renwick, Frank Forster, Sunnyside, Weald-road, Brentwood, Essex
1909			Resker, Herbert Charles, B.A. (Cantab.), c/o Messrs. Butterfield & Swire, Hong Kong
1902	Trans.		Revis, Cecil, 5, Carlton-villas, Station-road, Barnes, S.W.
1914			Reynard, Herbert Corner, B.Sc. (Lond.), Craiglea, Chase Green-avenue, Enfield, Middlesex
1873	Trans.	V.P. 1881-4, 89-92, 97-1900 P. 1901-1903.	Reynolds, James Emerson, Prof., Hon. Sc.D. and Hon. M.D. (Dub.), M.R.C.P. (Ireland), L.R.C.P. and S. (Edin.), F.R.S., 3, Inverness-gardens, Kensington, W.
1898	Trans.		Reynolds, William Colebrook, B.Sc. (Lond.), Wharfdale, Engayne-gardens, Upminster, Romford
1908	Trans.		Rhead, Ezra Lobb, M.Sc. Tech. (Manc.), F.I.C., Stonycroft, Polygon-avenue, Levenshulme, Manchester
1915			Rhodes, Henry Taylor Fowkes, 34, Newman-road, Erdington, Birmingham
1907			Rhodes, Percy Joseph, Bridge House, Church, Lancs.
1898	Trans.		Rich, Edward Milton, 211, King's Hall-road, Beckenham
1889			Richards, Duncan Taylor, 57, Osborne-avenue, Westoe-lane, South Shields
1889			‖Richards, Edgar, 60, Ayrault-street, Newport, Rhode Island, U.S.A.
1908			Richards, Francis Edward, B.Sc. (Lond.), A.R.C.S., County Secondary School, Redruth
1889			‖Richards, Percy Andrew Ellis, F.I.C., Thurn Lodge, Upper Richmond-road, Roehampton, S.W.; and Analytical Laboratories, Royal Dental Hospital, Leicester-square, W.C.
1886			Richards, William, B.Sc. (Lond.), 58, Thrale-road, Streatham, S.W.
1888	Trans.		‖Richardson, Clifford, A.B. (Harvard), M. Am. Soc. C.E., Room 1615, Woolworth Building, New York City, U.S.A.

Date of Election.		
1906		‖Richardson, Frederic Ion, B.A. (Cantab.), Rossmore, Molesworth-street, Kew, Melbourne, Australia
1883		Richardson, Frederic William, F.I.C., County Analyst's Office, Bradford
1888		Richardson, Hubert Naylor Bardsley, B.A. (Cantab.), 10, Friar-lane, Leicester
1911		Richardson, John Ffraid, Government Quinine Factory, Naduvatam P.O., The Nilgiris, Madras, India
1892		Richardson, Reginald Edensor Stanley, 10, Friar-lane, Leicester
1887	Trans.	Richmond, Henry Droop, F.I.C., c/o Boots Pure Drug Co., Technical Laboratory, Island-street, Nottingham
1912		Rideal, Eric Keightley, M.A. (Cantab.), Ph.D. (Bonn), A.I.C., The Châlet, Elstead, Godalming, Surrey
1882	Trans.	‖Rideal, Samuel, D.Sc. (Lond.), F.I.C., 28, Victoria-street, Westminster, S.W.
1910		Ridgway, Joseph, B.A. (Cantab.), Rownall Hall, Wetley Rocks, Stoke-on-Trent
1882	Trans.	‖Ridsdale, Charles Henry, F.I.C., 3, Wilson-street, Middlesbrough
1911		Ridsdale, Noël Douglas, Ravenscroft, Roman-road, Linthorpe, Middlesbrough
1905		Rigby, Thomas, Station Hotel, Dumfries
1898		Rigg, Gilbert, c/o Associated Smelters Proprietary, Ltd., Collins House, Collins-street, Melbourne, Australia
1914		Riley, Conly Hunter, Anchorage, Clayton-le-Moors, Accrington
1904		Riley, Louis John Eczekiel, F.I.C., 8, Newton-road, W.
1900		Riley, Walter Alfred, 100, King-street, Norwich
1893		Rintoul, William, F.I.C., Lauriston, Ardrossan, Ayrshire
1909		Ritchings, Walter, M.Sc. (Manc.), The Cowley School, St. Helens
1911	Trans.	Rivett, Albert Cherbury David, M.A. and B.Sc. (Oxon.), D.Sc. (Melbourne), The University, Melbourne, Australia
1907	Trans.	Rixon, Frederic William, M.Sc. (Vict.), Ph.D. (Giessen), 93, Cromwell-road, Bristol
1908		Roach, William Frothingham, M.D. and M.S. (Montreal), M.D. *ad eumdem* (McGill), D.P.H. (Oxon.), L.A.H. (Dub.), 7, Hill-street, Knightsbridge, S.W.
1902		Roast, Harold James, c/o Messrs. James Robertson and Co., Ltd., 142, William-street, Montreal, Canada
1893		Robbins, James Henry, B.Sc. (Lond.), 19, Argyle-road, Ilford
1914	Trans.	Roberts, Charles Edward, B.A. (Cantab.), B.Sc. (Lond.), 18, Wolverhampton-street, Dudley
1915		Roberts, David Charles, 32, Cavendish-drive, Rock Ferry, Birkenhead
1883		‖Roberts, Frederick George Adair, Chemical Works, Carpenter's-road, Stratford, E.

Date of Election.		
1899		Roberts, James, jun., 6, Rokeby-terrace, Hillhead, Glasgow
1876		Roberts, Martin Fenn, 137, Victoria-street, S.W.
1894		Roberts, Thomas John, Ingleside, Park-road, Huyton, Liverpool
1912	Trans.	Roberts, Walter Morrell, M.Sc. (Manc.), F.I.C., 66, Hampton-road, Forest Gate, E.
1894		Robertson, Archibald Blair, 39, Westbury-road, Bristol
1915		Robertson, George Scott, M.Sc. (Dun.), East Anglican Institute of Agriculture, Chelmsford
1914		Robertson, Joseph Drummond, Rev., The Church House, Troon, Camborne
1903	Trans.	Robertson, Philip Wilfred, M.A., M.Sc., (N.Z.), M.A. (Oxon.), Ph.D. (Leipzig), 22, Acacia-road, St. John's Wood, N.W.
1907	Trans.	Robertson, Robert, M.A. and D.Sc. (St. Andrews), F.I.C., Research Department, Royal Arsenal, Woolwich, S.E.; and 29, Charlton-road, Blackheath, S.E.
1901	Trans.	Robertson, William, 21, Worfield-street, Battersea Park, S.W.
1889		Robins, Harry Hollis, c/o Messrs. Southwell and Co., Dockhead, S.E.
1903		Robinson, Archibald Louis, Surgeon, R.N., M.A. and M.B. (Dub.), St. Maur, Palmerston-park, Dublin
1915		Robinson, Arthur Dawes, B.A. (Cantab.), Burrakur Ironworks, Kulti (E.I.R.), Bengal, India
1913		Robinson, Arthur Samuel, B.Sc. (Manc.), 1, Deeside-parade, West Kirby, Birkenhead
1915		Robinson, Fred, B.Sc. (Leeds), 41, Meldon-terrace, Heaton, Newcastle-on-Tyne
1914		Robinson, Frederic, M.Sc.Tech., F.I.C., The Hollies, Mile-End, Stockport
1909	Trans.	Robinson, Frederic William, M.Sc. (L'pool.), c/o The Hanovia Chemical and Manufacturing Co., 233, N.J.R.R.-avenue, Newark, N.J., U.S.A.
1896		Robinson, Henry Fishwick, M.Sc. (Vict.), 334, Droylsden-road, Newton Heath, Manchester
1882	Trans.	‖Robinson, Henry Haliburton, M.A. (Oxon.), F.I.C., 42, Penywern-road, Earl's Court, S.W.
1895		‖Robinson, Herbert Lewin, 1a, Middle Temple-lane, E.C.
1906		Robinson, Reginald Ernest, B.A. (Cantab.), The Villas, Stoke-on-Trent
1909	Trans.	Robinson, Robert, Prof., D.Sc. (Manc.), Lance House, Childwall-road, Wavertree, Liverpool, and Chemical Department, The University, Liverpool
1911	Trans.	‖Robison, Robert, Ph.D. (Leipzig), B.Sc. (Lond.), F.I.C., The Lister Institute, Chelsea Gardens, S.W.

Date of Election.			
1914			Robson, William Pawson, B.A. (Cape of Good Hope), Ph.D. (Halle), 78, Rolland-street, Cape Town, S. Africa
1904			Rodger, Robert, 4, Stevenage-road, Bishop's-park, Fulham, S.W.
1898			Rofe, Henry John, M.A. (Oxon.), 8, Victoria-street, Westminster, S.W.
1883			Rogers, Arthur William, Tadcaster Tower Brewery Co., Tadcaster
1916			Rogers, Conrad Howard, 114, Richmond-hill, Langley, Birmingham
1905			Rogers, Harold Rudolf, M.A. (Oxon.), The Limes, Albert-street, Newcastle-under-Lyme, Staffs.
1909			Rogers, Herbert, c/o Messrs. James Lyne Hancock, Ltd., 266, Goswell-road, E.C.
1914			Rogers, John, F.I.C., 195, West George-street, Glasgow
1903			Rogers, William David, B.Sc. (Lond.), A.R.C.S., F.I.C., Mandalay, Gerald-street, Wrexham
1906	Trans.		Rogerson, Harold, M.Sc. (Manc.), The Moorings, Walton-road, Sidcup, Kent
1913			Rolfe, Benedict Hugh, M.A. (Oxon.), The Eyrie, Crown Hill, Upper Norwood, S.E.
1894			Rolfe, John F., 71, Bristol-road, Edgbaston, Birmingham
1903			Roose, Fitzroy Owen Jonathan, Assoc.Inst.E.E., c/o The São Paulo Tramway Light and Power Co., Ltd., São Paulo, Brazil
1912			Roper, Herbert Carr, 42, Cavendish-place, Newcastle-on-Tyne
1910			Rose, John George, Government Analytical Laboratory, Cape Town, S. Africa
1891	Trans.	C. 1897-8.	‖Rose, Sir Thomas Kirke, D.Sc. (Lond.), F.I.C., Royal Mint, E.
1896	Trans.		Rosenheim, Otto, Ph.D. (Würzburg), 75, Hampstead-way, Hendon, N.W.
1913			Roskin, Hermann Horace, B.Sc. (Wales), 11, Newlands-road, Middlesbrough
1894			‖Ross, Arthur, F.I.C., 1, Glengall-road, Old Kent-road, S.E.
1905			Ross, Frederick Wilson Montrose, c/o St. Williams Fruit Preserves, Ltd., St. Williams, Norfolk County, Ontario, Canada
1896			Ross, Raymond St. George, F.I.C., Public Analyst's Office, Burnley
1902			Ross, William Charles, Capt., I.M.S., M.B., Ch.B. and D.P.H. (Edin.), 65, Cluny-gardens, Edinburgh
1891	Proc.		Rossiter, Edmund Charles, F.I.C., Brougham, West Hagley, Stourbridge
1892			Rothwell, Charles Frederick Seymour, Messrs. Rajar, Ltd., Mobberley, Knutsford
1904			Rouillard, Marie Jean Louis Ernest, B.Sc. (Edin.), Mount Moreland, Natal, S. Africa
1914			Rowbottam, Walter Edward, 30, Gerard-road, Barnes, S.W.

Date of Election.			
1914			Roy, Chandra Bhusan, M.A. (Calcutta), Patna College, Bankipore, India
1915	Trans.		Roy, Charles Smart, Ph.D. (Jena), 4, Farnley-road, Chingford, N.E.
1899			Royal-Dawson, Henry, 155, Bradford-road, Huddersfield
1901			‖Royle, Charles Leonard, c/o The Cartavio Sugar Co., Hacienda Cartavio, Trujillo, Peru, S. America
1905			Royle, Harold Marmion, Store House, Gas Works, Beckton, North Woolwich
1909			Rudolf, Norman Scott, M.Sc. (Vict. and L'pool.), F.I.C., 12A, Royal Automobile Club, Pall Mall, S.W.
1872	Trans.		Ruffle, John, F.I.C., Musley, Ware, Herts.
1889	Trans.	C. 1903-05	Ruhemann, Siegfried, M.A. (Cantab.), Ph.D. (Berlin), F.R.S., The Elms, Adams-road, Cambridge
1915	Trans.		Rule, Howard Gordon, B.Sc. (Lond.), Ph.D. (Munich), Chemistry Dept., The University, Edinburgh
1883			Rumble, Charles, F.I.C., 169, Gleneldon-road, Streatham, S.W.
1914			Rundell, Percy Charles, Glenthorne, St. Alban's-crescent, Woodford Green
1908			Runeckles, Arthur Robert, B.Sc. (Lond.), A.C.G.I., c/o Messrs. Brotherton & Co., Ltd., Lonsdale Dock, Workington
1913			Rusby, Reginald William, 12, Blenheim-road, Redland, Bristol
1890			‖Russell, Edward, B.Sc. (Lond.), F.I.C., 28, Apsley-road, Clifton, Bristol
1898	Trans.	C. 1912-16	Russell, Edward John, D.Sc. (Lond.), Lawes Agricultural Trust, Rothamsted Experimental Station, Harpenden, Herts.
1901			Russell, James Bertram, B.Sc. (Lond.), Marston, Belsize-road, Worthing
1910			Russell, John, B.A. (Oxon.), 4, Kenbourne-grove, Sheffield
1896			‖Rutter, Thomas Francis, B.Sc. (Lond.), Ph.D. (Leipzig), Newcastle-under-Lyme
1894			Ryce, George, B.A. (R.U.I.), A.R.C.S., J.P., Irish Agricultural Offices of the Potash Syndicate, 23, Kildare-street, Dublin
1901	Trans.		Ryffel, John Henry, M.A. (Cantab.), B.Sc. (Lond.), F.I.C., 10, Grasmere-road, Muswell Hill, N.
1888			‖Sach, Albert John, Kelvedon, North-road, Ryde, N.S.W.
1896			Sage, Charles Edward, F.I.C., 10, London-street, Fenchurch-street, E.C.
1909	Trans.		Sageman, Philip John, Government Laboratory, Clement's Inn-passage, Strand, W.C.

Date of Election.		
1907		Sahni, Ruchi Ram, Prof., M.A. (Punjab), Government College, Lahore, India
1879	Trans.	‖Sakurai, Joji, Prof., Hon. D.Sc. (Tokio), Hon. LL.D. (Glas.), Science College, Imperial University, Tokio, Japan, viâ Siberia
1880		Salamon, Alfred Gordon, A.R.S.M., F.I.C., 1, Fenchurch-avenue, E.C.
1908		Salamon, Maurice Salamon, 79, Mark-lane, E.C.
1876		‖Salomons, Sir David Lionel, Bart., M.A. (Cantab.), Assoc. Inst.C.E., J.P., D.L., Broomhill, Tunbridge Wells; and 49, Grosvenor-street, W.
1916		Salter, John Beauchamp, Capt. A.S.C., Royal Automobile Club, Pall Mall, S.W.
1871		‖Salter, Mortyn John, F.I.C., Bank House, Mickleton, Campden, Glos.
1859		‖Salter, Thomas William, 193, Priory-road, West-hill, Hastings
1907	Trans.	Salway, Arthur Henry, D.Sc. (Lond.), Ph.D. (Leipzig), 59, Cavendish-drive, Rock Ferry, Birkenhead
1915		Sampataiengar, Nuggehally, Department of Agriculture, Bangalore, India
1902		Sampson, John William, Crosswell House, Harrowby-road, Grantham
1882		Samuel, William Cobden, Elmdale, 66, Croxted-road, West Dulwich, S.E.
1898	Trans.	‖Sand, Henry Julius Salomon, Ph.D. (Zürich), D.Sc. (Birm.), Sir John Cass Technical Institute, Jewry-street, Aldgate, E.C.
1900	Trans.	Sanders, James McConnell, c/o Cia Mexicana de Petroles, "El Aguila," S.A., Refineria de Petroles, Tampico, Tamps., Mexico
1904		Sanders, Percy Richard, West Cliffe, Seaford, Sussex
1888		Sanderson, John, F.I.C., c/o Messrs. B. S. Cohen, Ltd., Britannia Pencil Works, Neasden-lane, N.W.
1890		Saniter, Ernest Henry, Strafford Villa, Moorgate, Rotherham
1891		Sanyal, Abhayacharan, M.A. (Calcutta), Sonarpura, Benares, U.P., India
1892		Sarbadhicary, Satya-prasad, 1, College-street, Calcutta, India
1900		Sargeant, Fred Pilkington, College of Pharmacy, Clarendon-road, Leeds
1913	Trans.	Sastry, Sosale Garalapury, B.A. (Madras), c/o Messrs. Gerard Bros., Ltd., The Soap Works, Nottingham
1907		Saunders, George Joseph, B.E. (Sydney), Central Technical College, Brisbane, Queensland, Australia
1913		Saunders, William Gilbert, A.I.C., 34, Hanover-street, Liverpool
1908		Saunderson, William, B.Sc. (Dun.), Cooerwull Academy, Bowenfels, N.S.W.
1911		Saville, William Bristow, 35, North-side, Clapham Common, S.W.

Date of Election.			
1909			‖Sawbridge, Bartle Frere, M.A. (Oxon.), F.I.C., The Brewery, Chiswell-street, E.C.
1898			Sayer, Harold Charles, 3, King Edward-avenue, Dartford
1890			Sayers William Charles, 63, High-street, Lewisham, S.E.
1885			‖Scammell, Luther Robert, c/o Messrs. F. H. Faulding & Co., 54, King William-street, Adelaide, S. Australia
1912	Trans.		Scarborough, Harold Archibald, M.Sc. (Birm.), 32, Vicarage-road, Smethwick, BO., Staffs.
1915	Trans.		Scharff, Godfrey Edward, B.A. (Cantab.), Knockranny, Bray, Co. Wicklow, Ireland
1893	Trans.		Schidrowitz, Philip, Ph.D. (Berne), 57, Chancery-lane, W.C.
1888			‖Schieffelin, William Jay, Ph.B. (Columbia), 170, William-street, New York City, U.S.A.
1907			Schlienger, Charles, B.Sc. (Lond.), Acadia House, 273, Camden-road, N.
1892			‖Schofield, James Alexander, A.R.S.M., F.I.C., The University, Sydney, N.S.W.
1902			Scholes, William, Mount Sion, Radcliffe, Lancs.
1911			Scopes, Lionel Gowing-, 14, Carson-road, Dulwich, S.E.
1899	Trans.		Schryver, Samuel Barnett, D.Sc. (Lond.), Ph.D. (Leipzig), Imperial College of Science and Technology, S. Kensington, S.W.
1879	Trans.	C. 1897-9 S. 1899-1904 T. 1904-15 P. 1915-	‖Scott, Alexander, M.A. and Sc.D. (Cantab.), M.A. (Dun.), D.Sc. (Edin.), F.R.S., F.I.C., 34, Upper Hamilton-terrace, St. John's Wood, N.W.
1908			Scott, Andrew Laidlaw, F.I.C., Royal Gunpowder Factory, Waltham Abbey, Essex
1901			Scott, George Charlton, c/o Messrs. Burn & Co., Ltd., Howrah Ironworks, Bengal, India
1905			Scott, John Irwin, M.A. (Oxon.), The Grammar School, Kettering
1906			Scouller, Walter Daly, M.Sc. (Leeds), B.Sc. (Vict.), Corporation Sewage Works, Sealand, Chester
1883	Proc.		Scudder, Frank, F.I.C., 44, Mosley-street, Manchester
1896			Seabrooke, Herbert Cecil, F.I.C., Black Ash, Grays, Essex
1912			Seal, Kunjo Behary, 5, Nilmony Dutt-lane, Calcutta, India
1914			Seal, Lall Behary, 3, Stewart-road, Cant P.O., Rangoon, Burma
1891			Searl, Albert, 7, Palmeira-avenue, Westcliff-on-Sea, BO., Southend-on-Sea
1905			Seaton, William Dunham, 40, Argyle-road, Ilford
1909	Trans.		Segaller, David, D.Sc. (Lond.), Ph.D. (Zürich), A.R.C.S., 146, Halifax Old-road, Huddersfield
1898	Trans.		Seligman, Richard, Ph.D. (Heidelberg), A.C.G.I., Oakwood, Oxshott-road, Leatherhead

Date of Election.			
1875			Sellon, John Scudamore, 78, Hatton-garden, E.C.
1910			Sen, Aswini Kumar, B.A. (Calcutta), B.Sc. (Vict.), The Bengal Luxmi Mills, Serampore, near Calcutta, India
1904	Trans.		Sen, Jatindra Nâth, M.A. (Calcutta), Department of Agriculture, Pusa, Behar and Orissa, India
1914			Sen, Rajkumar, Prof., M.Sc. (Calcutta), 14/3, Manicktola-street, Calcutta, India
1910	Trans.		Sen, Rajendra Nath, Prof., M.A. (Calcutta), M.Sc. (Leeds), Engineering College, Sibpur, Calcutta, India
1915			Sen, Ramtaran, L.M.S. (Calcutta), Provincial Bacteriological and Chemical Laboratory, Shillong, Assam, India
1875	Trans.		‖Senier, Alfred, Prof., Hon. D.Sc. (R.U.I.), M.D. (Mich.), Ph.D. (Berlin), F.I.C., 28, Herbert-park, Donnybrook, Dublin
1906			Senior, John, c/o Messrs. Morgan, Crossley & Co., Ltd., Ducie Mills, Miles Platting, Manchester
1903	Trans.	C. 1914-	Senter, George, D.Sc. (Lond.), Ph.D. (Leipzig), F.I.C., Birkbeck College, Bream's Buildings, Chancery-lane, E.C.
1896			Severn, Walter Dalrymple, A.R.C.S., Public Health Laboratory, Cape Town, S. Africa
1915			Sewell, John, 166, Victoria-street, S.W.
1907			Sewell, William George, B.Sc. (Lond.), Bournemouth School, Bournemouth
1874			‖Sexton, Alexander Humboldt, Prof., F.I.C., F.R.S.E., c/o The Librarian, The Technical College, 204, George-street, Glasgow
1895	Trans.		Seyler, Clarence Arthur, B.Sc. (Lond.), F.I.C., The Technical Institute, Nelson-terrace, Swansea
1904			Shacklady, Thomas George, Hope House, Cliffe-at-Hoo, Rochester
1880			Shadwell, John Emilius Lancelot, F.I.C., Osborne House, Bathwick-terrace, Bath
1874			Sharman, William, 52, Ickburgh-road, Clapton, N.E.
1910			Sharpe, Frederic Herbert, The Ferns, Cressington Park, Liverpool
1895			Sharrott, Thomas Chilwell, B.A. (Dub.), A.R.C.S., F.I.C., 27, Beresford-road, Chingford, N.E.
1895	Trans.		‖Shaw, George Elliott, B.Sc. (Lond.), F.I.C., Mungpoo P.O., Sonada, D.H. Railway, Bengal, India
1908	Trans.		Shaw, William Bayliss, M.A. and B.Sc. (Oxon.), Lonsdale House, Walsall
1912			Shaw, William Daveridge Hamilton, B.Sc. (Wales), c/o The Coppee Coke Oven Co., Ltd., King's House, Kingsway, W.C.
1887			Sheard, John Tomlinson, Birley Carr, Sheffield
1897			Shenton, James Porter, 37, Torbay-road, Chorlton-cum-Hardy, Manchester

Date of Election.		
1907	Trans.	Shepheard, Frederick George, D.Sc. (N.U.I.), B.Sc. (Lond.), A.R.C.S., F.I.C., Hetland Cottage, Ruthwell, Dumfriesshire
1899	Trans.	Shepheard, William Frederick John, 12, Bridge-street-row, Chester
1906		Shepherd, Arthur Burton, B.Sc. (Vict.), F.I.C., c/o The British Oil and Cake Mills, Ltd., Copenhagen Mill, Limehouse, E.
1874		‖Shepherd, Harcourt Henry Benjamin, F.I.C., 8, The Park, Sidcup, Kent
1899		Shepherd, John William, B.Sc. (Lond.), 23, Stanley-road, Wimbledon, S.W.
1901	Trans.	Sheppard, Samuel Edward, D.Sc. (Lond.), 191, Alameda-street, Rochester, N.Y., U.S.A.
1901		Shepperson, William, Deerswood, Crawley
1891	Trans.	‖Shields, John, D.Sc. (Edin.), Ph.D. (Strassburg), F.I.C., 4, Stanley-gardens, Cricklewood, N.W.
1908		Shilstone, Herbert Maxwell, B.Sc. and D.P.H. (Tulane), 402, Wells Fargo Building, New Orleans, U.S.A.
1896		Shimomura, Kotaro, Prof., Shinkarasumaru Kojinguchi Sagaru, Kyoto, Japan
1913		Shrewsbury, Herbert Sutcliffe, F.I.C., Government Laboratory, Trinidad, British West Indies
1904		Shrubsole, Alfred, 16, The Grove, Golders Green, N.W.
1915		Shulman, Harry, B.Sc. (Lond.) A.I.C., 21, Tredegar-square, Bow, E.
1886		Shutt, Frank Thomas, M.A. (Toronto), F.I.C., Experimental Farm, Ottawa, Canada
1890		Shuttlewood, Willis Brewin, 78, Whitehall-park, Hornsey-lane, Highgate, N.
1894		Shuttleworth, Edward Buckingham, Prof., 220, Sherborne-street, Toronto, Canada
1904		Siau, Raymond Louis, 15, Merridale-lane, Wolverhampton
1903		Sibley, Samuel Edward, c/o Messrs. Mauri Bros. and Thomson, Ltd., Castlereagh-street, Sydney, N.S.W.
1889		Sibson, Alfred Edward, 92, Lansdowne-place, Hove, BO., Brighton
1903		Siddle, George, Middleton-one-row, Co. Durham
1902	Trans.	‖Sidgwick, Nevil Vincent, M.A. (Oxon.), Sc.D. (Tübingen), Lincoln College, Oxford
1900	Trans.	Silberrad, Oswald, Ph.D. (Würzburg), Buckhurst Hill, Essex
1886		Silvester, Harry, B.Sc. (Birm.), F.I.C., 78, Holy Head-road, Handsworth, Birmingham
1899	Trans.	Simmonds, Charles, B.Sc. (Lond.), Airdrie, 61, Cottenham-park-road, Cottenham-park, Wimbledon, S.W.
1889		Simmonds, Henry, Engineer's Office, Gas Works, and Elton View House, Bury

Date of Election.		
1887		‖Simmons, Leonard Owen, 15, Leigham Court-road, Streatham Hill, S.W.
1905		Simmons, William Herbert, B.Sc. (Lond.), Oakleigh, Stoke Newington Common, N.
1895		Simons, Albert Joseph, c/o M. Simons, Esq., 31, Little Britain, E.C.
1906	Trans.	Simonsen, John Lionel, Prof., D.Sc. (Manc.), Presidency College, Madras, India
1896		Simpson, Aitken Megget, 444, Chester-road, Manchester
1902		Simpson, Duncan Ivan Rennard, 10, Brynmill-crescent, Swansea
1897		Simpson, Edward Sydney, B.E. (Sydney), B.Sc. (W.A.), Geological Survey Laboratory, Museum-street, Perth, Western Australia
1886	Proc.	‖Simpson, William Selby, F.I.C., The Gables, Cannon-hill, Southgate, N.
1913	Proc.	Simpson, William Slessor, M.A. and B.Sc. (Aberd.), Durban Roodeport Deep G. M. Co. Ltd., Village Deep, Johannesburg, Transvaal, S. Africa
1910		Sinclair, St. Clair Overbeek, M.A. (Cape of Good Hope), Government Analytical Laboratory, Parliament-street, Cape Town, S. Africa
1902	Proc.	Sindall, Robert Walter, 315, Brownhill-road, Catford, S.E.
1889		Singer, Ignatius, 3, Parkfield-road, Manningham, Bradford
1912	Trans.	‖Singh, Bawa Kartar, Prof., M.A. (Cantab.), Dacca College, Dacca, Bengal, India
1908		Singh, Puran, The Forest Research Institute, Dehra Dun, U.P., India
1902	Proc.	Sinnatt, Frank Sturdy, 321, Great Clowes-street, Higher Broughton, Manchester
1896		‖Sircar, Amrita Lal, 51, Sankaritola, Calcutta, India
1912	Trans.	Sircar, Anukul Chandra, M.A., Ph.D. (Calcutta), Dacca College, Dacca, Eastern Bengal, India
1902		Skertchly, William Pearson, F.I.C., 11, Billiter-square, E.C.
1888	Trans.	Skinner, Sidney, M.A. (Cantab.), South Western Polytechnic, Manresa-road, Chelsea, S.W.
1892		Skurray, Thomas, United Breweries, Abingdon, Berks.
1912		Sladden, Cyril Edgar, 12, Charleville-circus, Sydenham, S.E.
1910	Trans.	Slade, Roland Edgar, D.Sc. (Vict.), University College, Gower-street, W.C.
1879		Slater, Charles, M.A. and M.B. (Cantab.), M.R.C.S. (Eng.), 81, St. Ermin's-mansions, Westminster, S.W.
1880	Trans.	‖Slater, Harold Humboldt, F.I.C., Club de Residentes Extranjeros, Buenos Ayres, Argentine, S. America
1914		Slater, William Kershaw, B.Sc. (Manc.), Eastdene, Chamber-road, Shaw, Oldham

Date of Election.			
1903	Trans.		Slator, Arthur, Ph.D. (Leipzig), D.Sc. (Birm. and Lond.), F.I.C., 174, Ashby-road, Burton-on-Trent
1878			‖Slatter, George William, A.R.C.S.I., F.I.C., 241, Carlton-terrace, Nab Wood, Shipley
1895			Slocum, Frank Leroy, Ph.D. (Strassburg), 401, South Linden-avenue, E.E., Pittsburg, Pa., U.S.A.
1912	Trans.		Smart, Bertram James, B.Sc. (Lond.), Government Testing Office, Lithgow, N.S.W.
1875			‖Smetham, Alfred, F.I.C., 16, Brunswick-street, Liverpool
1898	Trans.	S. 1912-	‖Smiles, Samuel, D.Sc. (Lond.), University College, Gower-street, W.C. ; and The Quarry, Sanderstead-road, S. Croydon
1883			Smith, Adolphe, 12, Crookham-road, Fulham, S.W.
1890	Trans.		‖Smith, Alexander, Prof., Ph.D. (Munich), B.Sc. (Edin.), Department of Chemistry, Columbia University, New York City, U.S.A.
1888			Smith, Angus, F.I.C., 7, Eldon-street, Greenock
1911			Smith, Bernard Charles, 97, Bethune-road, Stamford Hill, N.
1906			Smith, Charles, Knowsley-road, Smithills, Bolton
1904	Trans.		Smith, Clarence, D.Sc. (Lond.), The Sun House, Harmondsworth, Yiewsley, Middlesex
1894	Trans.		Smith, Claude, F.I.C., Barngarth, Cartmel, Grange-over-Sands, Lancs.
1884			‖Smith, Edgar Francis, Trelawny, 21, Fairfax-road, Bedford Park, W.
1910			Smith, Ernest William, B.A. and B.Sc. (Lond.), A.I.C., 20, St. Bevan's-road, Halifax
1906			Smith, Frank, B.Sc. (Vict.), 415, Church-road, Smithills, Bolton
1896			Smith, George Egerton Scott-, F.I.C., 67, Surrey-street, Sheffield
1892			‖Smith, George Percy Darnell-, B.Sc. (Lond.), F.I.C., Biological Branch, Mining Museum, George-street-north, Sydney, N.S.W.
1912	Trans.		Smith, Henry Edgar, M.Sc. (Birm.), 90, Lightwoods Hill, Warley, Birmingham
1896	Trans.		Smith, Henry George, The Technological Museum, Sydney, N.S.W.
1904			Smith, Henry Heron, F.I.C., Tower House, Belvedere, Kent
1909	Trans.		Smith, Henry Llewellyn, B.Sc. (Manc.), F.I.C., Pharmaceutical Society, 17, Bloomsbury-square, W.C.
1878			Smith, Henry Russell, F.I.C., 1, Aubert-park, Highbury, N.
1900			‖Smith, Herbert Procter, Highfield, Shotton, Flints.
1901			Smith, James, Sunnyside, Groes-road, Cressington, Liverpool
1903			Smith, James Cruickshank, B.Sc. (Aberd.), King's House, King-street, E.C.
1910			Smith, James Harry, 9, High-street, Rishton, Blackburn
1911	Trans.		Smith, John Henry, Talleres F.C.C.A., Officina de Locomotoras, Rosario-de-Santa Fé, Argentine, S. America

Date of Election.			
1879			‖Smith, John William, 7, Brookfield-street, Roslindale, Boston, Mass., U.S.A.
1914			Smith, Joseph de Carle, B.Sc. (Lond.), Oak House, Newmarket-road, Norwich
1913			Smith, Montagu George, 8, Cross-road, Bromley Common, Bromley, Kent
1901	Trans.		Smith, Norman, D.Sc. (Vict.), The University, Manchester
1910			Smith, Percy Lancelot James, M.A. (Oxon.), F.I.C., Loretto School, Musselburgh
1912			Smith, Richard Coupe, 36, Mayfield-grove, Gorton, Manchester
1902			Smith, Robert Ely Blake, B.Sc. (Lond.), The Red House, Belvedere-avenue, Wimbledon-hill, Wimbledon, S.W.
1897			Smith, Robert Francis Wood, 90, Lower Thames-street, E.C.
1891			Smith, Robert Greig-, D.Sc. (Edin.), M.Sc. (Dun.), Linnean Society's House, Elizabeth Bay, Sydney, N.S.W.
1907			Smith, Robert Harry, Apsley House, Priory-road, Sheffield
1907			Smith, Robert Low, c/o Messrs. Vickers, Sons and Maxim, Ltd., Erith, Kent
1888			Smith, Samuel, 132, High-street, Tonbridge
1915	Trans.		Smith, Sydney, Ph.D. (Kiel), B.Sc. (Lond.), F.I.C., 2, Sunbeam Cottage, Dartford Heath, Dartford
1907			‖Smith, Sydney William, B.Sc. (Lond.), A.R.S.M., The Royal Mint, E.
1912	Trans.		Smith, Thomas Alfred, B.Sc. (Lond.), F.I.C., 91, Balsall Heath-road, Edgbaston, Birmingham
1910			Smith, Thomas May, c/o Messrs. A. Boake, Roberts & Co., Ltd., Carpenter's-road, Stratford, E.
1915			Smith, Vincent Harold, Penlee Villa, Warwick-road, West Drayton, Yiewsley, Middlesex
1866	Trans.		Smith, Watson, F.I.C., 34, Upper-park-road, Haverstock Hill, N.W.
1876			‖Smith, William Alexander, M.A. and M.B. (Oxon.), M.R.C.S. (Eng.), 70, Pembroke-road, Clifton, Bristol
1912			Smith, William Charles, Church-lane, Lowton, Newton-le-Willows
1910			Smith, William James Pittock, Emerald House, Carlyle-road, South Ealing, W.
1883	Trans.	{C. 1896-1900. V.P. 1905-08}	‖Smithells, Arthur, Lieut.-Col., B.Sc. (Lond.), F.R.S., F.I.C., G.H.Q., Home Forces, Horse Guards, S.W.
1908	Trans.		Smythe, John Armstrong, D.Sc. (Dun.), Ph.D. (Göttingen), Armstrong College, Newcastle-on-Tyne
1902			Smythe, John Seabury, M.Sc. (Vict.), Ph.D. (Würzburg), 22, Rawlinson-road, Hesketh-park, Southport

Date of Election.		
1887	Trans.	‖Snape, Henry Lloyd, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C., Balholm, Lathom-road, Southport
1887		Soane, Charles Emile, F.I.C., 31, Mattison-road, Hornsey, N.
1899	Trans.	Soddy, Frederick, Prof., M.A. (Oxon.), F.R.S., Marischal College, and 14, Albyn-terrace, Aberdeen
1891		Solomon, Frank Oakley, Dauntsey's Agricultural School, West Lavington, Littleton Pannel, Wilts.
1916		Solomon, Simon, 111, Sandringham-road, Dalston, N.E.
1898		‖Somerville, Henry, B.Sc. (Lond.), M.R.C.S. and L.R.C.P. (Lond.), Harrold, Sharnbrook, Beds.
1906		‖Sommerville, David, B.A. (R.U.I.), M.D., B.Ch., and D.P.H. (Cantab.), M.R.C.P. (Lond.), 31, Manor House, Marylebone-road, N.W.
1893		Sorrell, Henry Thomas, B.Sc. (Lond.), 54, Newcombe-road, Polygon, Southampton
1875		Southall, Alfred, Garrick House, Richmond Hill, Edgbaston
1897	Proc.	‖Southerden, Frank, B.Sc. (Lond.), F.I.C., Royal Albert Memorial College, Exeter
1883		Soward, Alfred Walter, C.B., 28, Therapia-road, Honor Oak, S.E.
1892		Spackman, Charles, Rosehaugh, Clitheroe
1908		Speed, John Day, 206, Hertford-road, Waltham Cross
1905		Speight, William Ewart, Corporation Sewage Works, Bolton
1883		‖Spencer, Ernest Samuel, 181, Drummond-road, Southwark Park, S.E.
1906	Trans.	Spencer, James Frederick, D.Sc. (L'pool.), B.Sc. (Vict.), Ph.D. (Breslau), F.I.C., Bedford College for Women, York-gate, Regent's Park, N.W.
1886		Spencer, Richard, 242, Dalton-road, Barrow-in-Furness
1894		Spenzer, John George, Prof., M.D. (Ohio), Ph.D. (Strassburg), Ohio Wesleyan University, 1825, East 93rd-street, N.E., Cleveland, Ohio, U.S.A.
1904		Spielmann, Percy Edwin, B.Sc. (Lond.), Ph.D. (Bâle), A.R.C.S., F.I.C., Arts Club, 40, Dover-street, W.
1908		Spiers, Charles Sedgley, Beaudesert, Queensland, Australia
1914		Spiers, Henry Michael, B.A. (Cantab.), B.Sc. (Lond.), 34, Brondesbury-road, Kilburn, N.W.
1859	Trans.	‖Spiller, John, F.I.C., 2, St. Mary's-road, Canonbury, N.
1863		‖Spiller, William, F.I.C., 2, Lindfield-gardens, Hampstead, N.W.
1885		‖Spottiswoode, William Hugh, Balliol College, Oxford; and 6, Middle New-street, E.C.
1906	Trans.	Sproxton, Foster, B.Sc. (Lond.), A.I.C., Brantham Works, Brantham, Manningtree, Essex
1882		‖Squire, Peter Wyatt, 413, Oxford-street, W.

Date of Election.		
1892		Squires, Alfred James, Greenbank, Coroner's-lane, Farnworth, Lancs.
1899		Stainer, John Ward, 103, Cheriton-road, Folkestone
1879	Trans.	‖Stallard, George, M.A. (Oxon.), Pra Oursi, Champ de Praz, Val d'Aosta, Italy
1914		Stamp, Charles Alfred, Passey's House, Eltham, S.E.
1911		Stanford, Robert Viner, Ph.D. (Kiel), M.Sc. (Birm.), B.Sc. (Lond.), Cardiff City Mental Hospital, Whitchurch, Cardiff
1904		Stanger, Reginald Harry Hursthouse, Chemical Laboratory and Testing Works, 2, Broadway, Westminster, S.W.
1902		Stanger, William Charles South, Ambleside, Corder-road, Ipswich
1898		Stannard, Oscar Julian, Ph.D. (Erlangen), 65, London-wall, E.C.
1887	Trans.	‖Stansell, Lionel William, F.I.C., 7, Albion-place, Maidstone
1895		‖Stansfield, Alfred, D.Sc. (Lond.), McGill University, Montreal, Canada
1902		Stansfield, Edgar, M.Sc. (Vict.), Fuel Testing Plant, Division-street, Ottawa, Canada
1913		Stansfield, William James, A.R.C.S., 23, Bell Hall-terrace, Savile-park, Halifax
1900	Trans.	Stapleton, Henry Ernest, Prof., M.A. and B.Sc. (Oxon.), The Club, Dacca, Eastern Bengal and Assam, India
1870		Starey, Arthur John, 39, Woodland-gardens, Highgate, N.
1870	Trans.	‖Stark, James Fleming, Rosedale, Bromborough, Cheshire
1908		Stead, Arthur, B.Sc. (Vict.), Grootfontein School of Agriculture, Middleburg, Cape Province, S. Africa
1902		Stead, Francis Bernard, 1, Thornton-hill, Wimbledon, S.W.
1896		Stead, John Christopher, 57, Chancery-lane, W.C.
1882	Trans.	Stead, John Edward, D. Met. (Sheffield), Hon. D.Sc. (Manc.), F.R.S., F.I.C., 11, Queen's terrace, Middlesbrough
1910		Stedman, Ernest, M.Sc. (Vict.), Upholland Grammar School, Orrell, Wigan
1885		‖Steel, Robert Elliot, Avoca, Newland, Sherborne
1900	Trans.	Steele, Bertram Dillon, Prof., D.Sc. (Melbourne), Department of Explosives Supplies, Ministry of Munitions, Storey's Gate, S.W.
1912	Trans.	Steele, Victor, 55, Amersham-road, New Cross, S.E.
1905		Steger, James, B.Sc. (Lond.), 10, Elmdale-road, Clifton, Bristol
1901		Stell, Samuel Fenton, 25, Henry-street, Keighley
1892	Trans.	‖Stenhouse, James, Broomieknowe House, Lasswade, Midlothian
1884		Stenhouse, Thomas, F.I.C., 166, Drake-street, Rochdale
1912		Stephen, Alfred Ernest, c/o The Chilean Nitrate of Soda Propaganda, P.O. Box 1197, and 67, Castlereagh-street, Sydney, N.S.W.
1895	Trans.	Stephens, Frank Robert, c/o Messrs. Idris, Pratt-street, Camden Town, N.W.
1880		‖Stephens, Henry Charles, Avenue House, Finchley, N.

Date of Election.		
1897		Stephens, Michael Edmund, 57, Aldersgate-street, E.C.
1910		Stephenson, Guy, Alexandra-terrace, Crook, Co. Durham
1895		Stephenson, Herbert Frederick, A.R.C.S., F.I.C., 8, Mitcham-park, Mitcham, Surrey
1901		Stephenson, Robert, jun., M.A. (Cantab.), Burwell, Cambridge
1891	Trans.	‖Stephenson, Thomas, F.R.S.E., 6, South Charlotte-street, Edinburgh
1888	Trans.	Stern, Arthur Landauer, D.Sc. (Lond.), F.I.C., 148, High-street, Burton-on-Trent
1881		‖Steuart, Daniel Rankin, Osborne Cottage, Broxburn, West Lothian
1896		Steuart, Douglas Stuart Spens, B.Sc. (Vict.), Bollowall, St. Just, Cornwall
1905		Stevens, Harold Blythen, F.I.C., Oxford Works, Tower Bridge-road, S.E.
1897	Trans.	Stevens, Henry Potter, M.A. (Oxon.), Ph.D. (Heidelberg), F.I.C., 15, Borough, S.E.
1903		Stevens, Montague White, A.R.C.S., F.I.C., 9, Burlington-avenue, Kew Gardens, BO., Surrey
1899		Stevenson, Arnold, B.A. (Cantab.), 4, Porchester-gardens, W.
1903	Trans.	Stevenson, Henry Edward, 22, Wilton-grove, Wimbledon, S.W.
1904		Stevenson, Henry Ernest, Avondale, Ditton Hill, Surrey
1909		Stevenson, James Thomas, 67, Surrey-street, Sheffield
1879		Stevenson, William, 95A, Southwark-street, S.E.
1908		Stewart, Alexander Mackintosh, c/o Mrs. A. M. Stewart, Cambridge House, St. Alban's-road, St. Anne's-on-the-Sea, Lancs.
1914		Stewart, Alan West, D.Sc. (Brussels), 29, Westbere-road, West Hampstead, N.W.
1903	Trans.	Stewart, Alfred Walter, D.Sc. (Glas.), 3, Annfield-road, Glasgow
1902		Stewart, Hector, Solai, Wagin, Western Australia
1907		Stobie, Harold Ramsay, 18–20, Broad-street House, New Broad-street, E.C.
1887		Stocks, Herbert Birtwhistle, F.I.C., 33, Prenton-park-road, Birkenhead
1879	Proc.	‖Stokes, Alfred Walter, F.I.C., 179, Edgware-road, W.
1911		Stokes, George Alfred, A.I.C., 179, Edgware-road, W.
1873		‖Stone, Edward Daniel, Ackersley, Cheadle Hulme, Stockport
1914		Stone, Horace Gilbert, B.Sc. (Lond.), 41, Queen's-road, High Wycombe
1875		‖Stone, John Frederic Matthias Harris, M.A. (Cantab.), Barrister-at-Law of the Western Circuit, 28, Charing Cross-road, W.C.; and Oxford and Cambridge Club, 17, Pall Mall, S.W.

Date of Election.		
1879		‖Stone, William, M.A. (Cantab.), United University, Garrick, Oxford and Cambridge, Bath, Albemarle, Hurlingham, Authors', Royal Societies, Automobile, and Reform Clubs; and 63, Curzon-street, Mayfair, W.
1909		Stones, George Bertram, M.Sc. (Manc.), The Technical School, Smethwick, BO., Staffs.
1906		Storey, Francis Wylie, B.Sc. (Lond.), Normal Training College, Bloemfontein, Orange Free State, S. Africa
1900		Storr, Bertram Vincent, M.Sc. (Vict.), 26, The Square, Garden Suburb, Ilford
1909		Strachan, James Thallon, c/o The Canada Paper Co., Ltd., Windsor Mills, Que., Canada
1904	Trans.	Streatfeild, Frederick Henry, 54, Belgrave-road, Wanstead, N.E.
1906		Streimer, Emanuel George, 4, Clova-road, Forest Gate, E.
1912		Strivens, Percy Rudolph, 20, Cartmell-road, St. Anne's-on-the-Sea, Lancs.
1909		Strohmenger, Arthur Percy, Caxton House, Westminster, S.W.
1900		Strong, Archie Hugh, 63, Herne-hill-road, Camberwell, S.E.
1904	Trans.	‖Struthers, Robert de Jersey Fleming-, M.A. and B.Sc. (Oxon.), Exeter College, Oxford
1885	Trans.	‖Stuart, Charles Maddock, M.A. (Cantab.), F.I.C., St. Dunstan's College, Catford, S.E.
1913	Trans.	Stuart, John McArthur, Ivy Bank, Liberton, Midlothian
1910		Stuart, Murray, Prof., D.Sc. (Birm.), Presidency College, Madras, India
1897	Trans.	Stubbs, George, F.I.C., Lingdale, Etchingham Park-road, Finchley, N.
1907		Sturrock, George Colleymore, Capt. R.A., Indian Cordite Factory, Aruvankad, Nilgiris, India
1890	Trans.	‖Sudborough, John Joseph, Prof., D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C., Indian Institute of Science, Bangalore, India
1878	Trans.	‖Suguira, Shigetake, c/o Tokyo Chemical Society, Science College, Imperial University, Tokyo, Japan
1911		Summers, George Douglas, Manor Lodge, Manor-road, East Molesey, Surrey
1887		‖Sutherland, David Alexander, F.I.C., 26, Victoria-street, Westminster, S.W.
1860		Sutton, Francis, F.I.C., Laboratory, Bank Plain, Norwich
1886		‖Sutton, Francis Napier, F.I.C., 21, Lydford-road, Cricklewood, N.W.
1894		‖Swinburne, James, F.R.S., M.Inst.C.E., 82, Victoria-street, S.W.
1891		Sykes, Matthew Carrington, M.D. (Dun.), F.R.C.S. (Edin.), M.R.C.S. (Eng.), L.R.C.P. and D.P.H. (Lond.), County Maynar Tower, Hemel Hempstead

Date of Election.		
1874	Trans.	‖Symons, William Henry, M.D. (Brux.), D.P.H. (Oxon. and Dun.), M.R.C.S. (Eng.), F.I.C., Health Office, Guildhall, Bath
1914		Tagg, Max Herbert, B.Sc. (Lond.), 17, Hardwick-road, Chiswick, W.
1881	Trans.	‖Takamatsu, Toyokichi, Prof., Engineering College, Imperial University, Tokyo, Japan
1887	Trans.	‖Takamine, Jokichi, 550, West 173rd-street, New York City, U.S.A.
1901		Tankard, Arnold Rowsby, F.I.C., 40, Lowgate, and 67, Ferens-avenue, Cottingham-road, Hull
1909		Taplin, Edward Walter, c/o Messrs. E. Lacon & Co., Ltd., The Brewery, Great Yarmouth
1909		Tapp, Charles, Cradock, Cape Colony, S. Africa
1901		Tatam, George William Gerald, 3, Courtney-road, Waddon, Croydon
1909		Tate, Arthur Edwin, M.Sc. (Dun.), 66, Earlham-road, Norwich
1908		Tate, Francis George Henry, 96, Barrow-road, Streatham, S.W.
1890		Tate, Francis Henry, 9, Hackins Hey, Liverpool
1881	Trans.	Tate, George, Ph.D. (Würzburg), F.I.C., Windsor Buildings, George-street, Liverpool
1884		‖Tate, Walter, Tresco, Bloomfield Park, Bath
1916		Tatham, Guy Thomas Percy, B.Sc. (Lond.), 120, Lower Baggot-street, Dublin
1867		Tatlock, Robert Rattray, F.I.C., Kilarden, Rosneath, Dumbartonshire ; and 156, Bath-street, Glasgow
1913		Tayler, Harold Frank, 105, Barrow-road, Streatham, S.W.
1905		Tayleur, John William, B.Sc. (Lond.), The Woodlands, Writtle, Chelmsford
1916		Taylor, Fred, Womersley-road, Knottingley, Yorks.
1882		Taylor, Gotfred Midgley, Caxton House, Westminster, S.W.
1894		Taylor, Herbert John, Dewsbury Technical School, Dewsbury
1880		‖Taylor, James, B.Sc. (Manc.), A.R.S.M., Cartref, Brierley-street, Mosman, N.S.W.
1891	Trans.	Taylor, John, 15, Lucius-street, Torquay
1915	Trans.	Taylor, John, M.Sc. (Vict.), University College, Cork, Ireland
1888		Taylor, John George, 3, Outram-street, Stockton-on-Tees
1874	Trans.	‖Taylor, Robert Llewellyn, F.I.C., 37, Mayfield-road, Whalley Range, Manchester
1901	Trans.	Taylor, William Henry, B.Sc. (Lond.), F.I.C., 36, Glenhouse-road, Eltham Park, Kent
1878		‖Tcherniac, Joseph, Ph.D. (Zürich), 49, Palace-road, Streatham Hill, S.W.

Date of Election.		
1879	Trans.	‖Teed, Frank Litherland, D.Sc. (Lond.), F.I.C., 9, Mincing-lane, E.C.
1906		Tempany, Harold Augustine, D.Sc. (Lond.), F.I.C., St. Johns, Antigua, British West Indies
1910	Trans.	Temperley, Claude Vareille, B.Sc. (Lond.), The Rectory, South Willingham, Lincoln
1914		Temple, Harold Edwin, Olton, Acock's Green, Birmingham
1901		Templeman, William Henry, B.A. and LL.M. (Cantab.), Staff Quarters, Sark Bridge, H.M. Factory, Gretna, Carlisle
1913		Tennant, Robert, 9, Princes-square, Strathbungo, Glasgow
1910		Terrey, Augustus George, Clematis Villa, Alexandra-road, South Woodford, N.E.
1915		Terrey, Henry, B.Sc. (Lond.), University College, Gower-street, W.C.
1894		‖Terry, Edwin, 374, Brixton-road, S.W.
1893		Thackrah, James Robert, M.A. (Oxon.), Ph.D. (Leipzig), Technical Schools, Tavistock-road, Plymouth
1895		Theodosius, Alfred Fletcher, M.A. (Oxon.), University College, Oxford
1912		Thévenaz, William, D.-ès-Sc. (Geneva), 48, Grey-street, Hull
1904		Thibault, Paul John, Eskbank Iron and Steel Works, Lithgow, N.S.W.
1910	Trans.	Thole, Ferdinand Bernard, D.Sc. (Lond.), Technical College, East Ham, E.
1901		Thomas, Albert Edward, B.Sc. (Lond.), F.I.C., Stanley House, Tavistock-road, Croydon
1913	Trans.	Thomas, Ebenezer Rees, B.A. (Cantab.), M.Sc. (Wales), Rugby School, Rugby
1908		Thomas, Frank Moreton, 33, King William-street, E.C.
1907	Trans.	‖Thomas, Frederick, M.Sc. (Manc.), c/o Messrs. Williams Bros. and Co., Colour Manufacturers, Hounslow; and 29, Fairhaven-road, St. Anne's-on-the-Sea, Lancs.
1905		Thomas, George Devenish, B.Sc. (Lond.), 4, Connaught Park-villas, Frith-road, Dover
1915		Thomas, Hugh Wolseley, 9, Dalhousie-square, Calcutta, India
1912		Thomas, William Leonard, 10, Victor-road, Bradford
1912		Thompson, Arthur, Parkfield Hall, Wolverhampton
1877		‖Thompson, Beeby, 67, Victoria-road, Northampton
1904		Thompson, Charles Herbert, Harrington House, Amblecote, Stourbridge
1886	Trans.	‖Thompson, Claude Metford, Prof., M.A. (Cantab.), D.Sc. (Lond.), University College, and 38, Park-place, Cardiff
1894		Thompson, Edward Cumming, Froyle House, Westcombe Park-road, S.E.

Date of Election.			
1893			‖Thompson, Frank Ernest, A.R.C.S., F.I.C., 23, Lichfield-street, Walsall
1893			Thompson, George Rudd, F.I.C., The Laboratory, 69, Dock-street, Newport, Mon.
1897			Thompson, Harry, Chemical Laboratory, 5, Bishop-lane, Hull
1913			Thompson, Percy James, The Avenue, Clytha-square, Newport, Mon.
1914			Thompson, Thomas William, M.A. (Cantab.), Kenilworth, Scatcherd-lane, Morley, Leeds
1886			Thompson, William Phillips, Rock Edge, Upper-park, Birkenhead
1911	Trans.		Thomson, David, Prof., M.A. and B.Sc. (Glas.), Ph.D. (Göttingen), Cotton College, Gauhati, Assam, India
1872	Trans.	C. 1880-3, 1904-06, 1914-16 S. 1883-98 V.P. 1898-1901	‖Thomson, John Millar, Emeritus Prof., Hon. LL.D. (Glas.), F.R.S., F.I.C., Beechcroft, Prestwood, Great Missenden, Bucks.
1912			Thomson, John Scott, c/o Messrs. Thomson & Co., Crawford-street, Dunedin, New Zealand
1899			Thomson, Robert Tatlock, F.I.C., 156, Bath-street, Glasgow
1872			Thomson, William, F.I.C., Royal Institution Laboratory, Manchester
1895			Thomson, William Thomas, "Stanton," Parkestone-road, Poole
1882	Trans.		Thorne, Leonard Temple, Ph.D. (Würzburg), F.I.C., Highlands, Belmont, Surrey
1913	Trans.		Thorne, Percy Cyril Lesley, B.A. (Cantab.), 22, Arbuthnot-road, New Cross Gate, S.E.
1906			Thornton, Percy Charles, 7, Sherard-gardens, Eltham, S.E.
1906			Thorp, Arthur William, Pavyotts' House, North Coker, Yeovil
1891			Thorp, Walter, B.Sc. (Lond. and Leeds), F.I.C., Sorrentoville, Dalkey, Co. Dublin
1871	Trans.	C. 1879-83 V.P. 1884-7 T. 1889-99 P. 1899-1901	†‖Thorpe, Sir Edward, Prof., C.B., D.Sc. (Vict.), Sc.D. (Dub.), Ph.D. (Heidelberg), LL.D. (Glas.), F.R.S., Whinfield, Salcombe, S. Devon
1893	Trans.	C. 1915-	Thorpe, Jocelyn Field, Prof., D.Sc. (Manc.), Ph.D. (Heidelberg), F.R.S., F.I.C., The Imperial College of Science and Technology, S. Kensington, S.W.
1899	Trans.	V.P. 1915-	Threlfall, Richard, Prof., M.A. (Cantab.), Assoc. M.Inst.C.E., F.R.S., Oakhurst, Church-road, Edgbaston, Birmingham
1897	Trans.		‖Tickle, Thomas, B.Sc. (Lond.), F.I.C., 83, Queen-street, Exeter
1916			Tidman, Cecil Francis, B.Sc. (Birm.), 1, Rockcliffe-terrace, Carlin How, Yorks.
1902			Tidy, Henry Letheby, M.A., M.B., and B.Ch. (Oxon.), M.R.C.S. (Eng.), M.R.C.P. (Lond.), 39, Devonshire-place, W.

† Longstaff Medallist, 1881.

Date of Election.			
1903			Tilburn, Charles, c/o The Australian Explosives and Chemical Co., Ltd., Deer Park, Victoria, Australia
1915			Tilden, Henry Burroughs, Poste Restante, Bombay, India
1865	Trans.	C. 1878-81 V.P. 85-8 91-94, 96-9 T. 1899-03 P.1903-05	‖Tilden, Sir William Augustus, Emeritus Prof., D.Sc. (Lond.), Hon. Sc.D. (Dub.), Hon. D.Sc. (Vict.), Hon. LL.D. (Birm.), F.R.S., F.I.C., The Oaks, Northwood, Middlesex
1912			Till, William Compton, M.Sc. (Birm.), 14, Minstead-road, Gravelly Hill, Birmingham
1900			Tilley, James Walter, 95A, Southwark-street, S.E.
1909			Tilley, Vernon James, F.I.C., 95A, Southwark-street, S.E.
1915			Ting, Su-Hian, B.Sc. (Lond.), 62, The Chase, Clapham Common, S.W.
1904	Trans.		Tingle, Alfred, B.Sc. (Aberd. and Lond.), Ph.D. (Penn.), Chemical Laboratory, Department of Customs, Ottawa, Ontario, Canada
1889	Trans.		‖Tingle, John Bishop, Prof., Ph.D. (Munich), McMaster University, Toronto, Canada
1909			Tingle, Joseph Grantley, Ruthven-street, Toowoomba, Queensland
1907	Trans.		Tinkler, Charles Kenneth, D.Sc. (Birm.), B.Sc. (Wales), King's College for Women, Campden Hill-road, W.
1898			‖Tisdale, Charles William Walker, The Dairy, Northallerton, Yorks.
1905	Trans.		Titherley, Arthur Walsh, D.Sc. (Vict. and L'pool.), Ph.D. (Heidelberg), The Tower, Llangollen
1909	Trans.		Tizard, Henry Thomas, M.A. (Oxon.), Oriel College, Oxford
1907			Toch, Maximilian, 52, Ninth-street, Long Island City, N.Y., U.S.A.
1891			Tocher, James Fowler, D.Sc. (Aberd.), F.I.C., County Laboratory, Crown Mansions, 41½, Union-street, Aberdeen
1884	Trans.		‖Tompson, Frederick William, The Bower, Limpsfield, Surrey
1877			‖Toms, Frederick Woodland, F.I.C., Official Analyst, Jersey
1904			Tong, Walter, 64, Belgrave-road, New Moston, Failsworth, Manchester
1906			Tonkin, Ronald William, 9, Ruvigny Mansions, Putney, S.W.
1907			Tonner, William Griffiths, B.Sc. (Wales), 22, Rugby-avenue, Neath, Glam.
1914			Tower, Olin Freeman, Prof., Ph.D. (Leipzig), Adelbert College Cleveland, Ohio, U.S.A.
1893			‖Towers, John William, Victoria-road, Widnes
1888			‖Townsend, Charles Frederick, Stotfold Bury, Baldock, Herts.
1903			Toyne, Francis Digby, M.A. (Cantab.), c/o Messrs. Kelsall and Kemp, Ltd., Woodhouse Mills, Norden, Rochdale

Date of Election.		
1887		‖Traphagen, Frank Weiss, Prof., Ph.D. (Columbia), Colorado School of Mines, Golden, Colorado, U.S.A.
1892	Trans.	Travers, Morris William, D.Sc. (Lond.), F.R.S., 17, Lexham-gardens, S.W.
1906		Treble, Richard Lumley, B.Sc. (Dun.), Larpool, Gordon-road, Shoreham-by-Sea, Sussex
1908		Trechmann, Adolph Octavius, The Old Palace, Rochester, Kent
1895		Trehärne, Frederick Gwilym, Wrangbrook, Llanishen, Cardiff
1915		Trehair, Warwick Oben Gurney, 34, Second-avenue, Greyville, Durban, Natal, S. Africa
1888		‖Trewby, Herbert, Kumra Lodge, Kelvedon Hatch, Brentwood
1881		‖Trigger, Oliver, F.I.C., Chemical Dept., Royal Arsenal, Woolwich, S.E.
1897		Tripp, Edward Howard, Ph.D. (Marburg), The Modern School, Bedford
1909		Truelove, Charles William, B.Sc. (Lond.), 23, Woodcote-road, Wanstead, N.E.
1912		‖Tsao, Hui Chun, Prof., B.Sc. (Birm.), Akademio Utopia (Tai Tung Shoh Yuan), north of S.H.R. Station, Shanghai, China
1916		Tschitschibabin, Alexej Euguenievitsch, Prof., Imperial Technical School, Moscow, Russia
1910	Trans.	Tschugaeff, Leo, Prof., The University, Petrograd, Russia
1905	Trans.	Tuck, William Bradshaw, D.Sc. (Lond.), University College, Gower-street, W.C.
1896		Tuckett, James Edwin Shum, M.A. (Cantab.), Marlborough College, Marlborough
1892		‖Tuer, Arthur Holt, Douglas House, Worthington, Wigan
1902		Tunnicliffe, William Wright, B.Sc. (Lond.), The Herbert Strutt School, Belper
1910		Turbutt, Richard Babington, Capt. R.A., B.A. (Oxon.), 50th Siege Battery, Royal Artillery, B.E.F., France
1897	Trans.	Turnbull, Andrew, Ph.D. (Heidelberg), 18, Hackin's Hey, Liverpool
1906	Trans.	Turnbull, Robert Hutchison, F.I.C., P.O. Box 289, 10, Strand-road, Calcutta, India
1903		Turner, Arnold, 35, Woodlands, Golders Green-road, Hendon, N.W.
1886		Turner, Arthur, The Limes, Aylesbury
1897		Turner, Basil William, 83, Pitt-street, Sydney, N.S.W.
1888	Trans.	Turner, Charles, Ivy Villa, Nursery-lane, Wilmslow, Manchester
1914	Trans.	Turner, Eustace Ebenezer, B.Sc. (Lond.), Sidney Sussex College, Cambridge
1906		Turner, George Augustus, 12, The Foregate, Worcester
1910		Turner, Joseph, Azo House, Birkby, Huddersfield

Date of Election.			
1883	Trans.		‖Turner, Thomas, Prof., M.Sc. (Vict.), A.R.S.M., F.I.C., The University, Birmingham
1903	Trans.		Turner, William Ernest Stephen, D.Sc. (Lond.), M.Sc. (Birm.), The University, Sheffield
1913			Turnill, Thomas Willoughby, c/o Atlas Preservative Co., Windmill-lane, Deptford, S.E.
1889	Trans.		Turpin, George Sherbrooke, M.A. (Cantab.), D.Sc. (Lond.), High School, Nottingham
1871			‖Tustin, John Robert, Albion House, The Marina, Deal
1888	Trans.	C. 1909-12	Tutton, Alfred Edwin Howard, M.A. and D.Sc. (Oxon.), F.R.S., Duart, Yelverton, Devon
1879			‖Tweedie, George Richard, 59, Church-road, Richmond, Surrey
1915			Twigg, Walter Ratledge, Beverley, Beech-hill, Luton
1907			Twiney, William George, B.Sc. (Lond.), 9, North-street, Kingston, Jamaica
1904	Trans.		Twiss, Douglas Frank, D.Sc. (Birm.), B.Sc. (Lond.), F.I.C., Glendevon, Royal-road, Sutton Coldfield, Birmingham
1913			Twomey, Jeremiah, M.Sc. (L'pool.), 21, Onslow-road, Elm-park, Liverpool
1899	Trans.		Tyler, Ernest Albert, M.A. (Cantab.), 33, The Promenade, Mount Pleasant, Swansea
1876			Typke, Paul George William, F.I.C., Lawn House, New Malden, Surrey
1876			Tyrer, Thomas, F.I.C., Stirling Chemical Works, Abbey-lane, Stratford, E.
1903			Tyrrell, Dennis, 182, King-street, Norwich
1908			Tyson, Thomas Marshall, 109, Carpenters-road, Stratford, E.
1915			Ullah, Mohammad Sana, B.A. and M.Sc. (Punjab), 11, Aberdeen-park, Highbury, N.
1915			Ullmann, Harry Maas, Ph.D. (Johns Hopkins), Lehigh University, South Bethlehem, Pa., U.S.A.
1865			Umney, Charles, F.I.C., 50, Southwark-street, S.E.
1893	Trans.		Umney, John Charles, 50, Southwark-street, S.E.
1889			‖Underhill, Thomas John, Stanley, 53, Lanercost-road, Tulse Hill, S.W.
1904			Underhill, William Wood, 10, Hartham-road, Holloway, N.
1897			‖Unwalla, Rustomji Navroji, Medical Dept., Bhaunagar, Kathiawâr, India
1912			Ure, Paul Jenner, c/o Messrs. Ure & Hylands, Wickham-street, Brisbane, Queensland, Australia
1909	Trans.		Usher, Francis Lawry, B.Sc. (Lond.), Central College, Bangalore, Mysore, India

Date of Election.			
1911			Vakil, Kapibram Hardevram, B.A. (Bombay), B.Sc. Tech. (Manc.), No. 5, Santa Cruz, Bombay, India
1890			Valentin, Basil William, Messrs. Buckley Bros., Brewery, Llanelly, S. Wales
1910			Vance, John Fleming Culun Brown, 947, Richard-street, Vancouver, British Columbia
1911	Trans.		Vanstone, Ernest, D.Sc. (Birm.), M.Sc. (Wales), Pembrey Factory, Nobel's Explosives Co., Ltd., Pembrey, Burry Port, Carmarthenshire
1909			Varley, Reginald Wells, c/o Leys Malleable Castings Co., Ltd., Derby
1883			Vasey, Samuel Archibald, F.I.C., Beechcroft, Burnt Ash-lane, Bromley, Kent
1911			Vassiliev, Alexey Mikhailovich, The University, Kasan, Russia
1879	Trans.		Veley, Victor Herbert, M.A. and D.Sc. (Oxon.), F.R.S., 8, Marlborough-place, N.W.
1891			Velling, Frederick William de, B.A. (Oxon.), Municipal Secondary School, The Boulevard, Hull
1881			Venable, Francis Preston, Ph.D. (Göttingen), Chapel Hill, North Carolina, U.S.A.
1887			‖ Vergara, Vargas José Maria, Apartado No. 120, Bogotá, Colombia, S. America
1901			Verteuil, Joseph de, Clarence-street, Port of Spain, Trinidad, British West Indies
1897			Viccajee, Framjee Khurshedjee, c/o The Andheri Industrials, Marol-road, Andheri, B.B.C.I.E., viâ Bombay, India
1908			Vidyant, Hari Prasad, M.A. (Allahabad), C.E., Executive Engineer, 52, Makbulganj-road, Lucknow, India
1915			Viraraghavan, Kadayam Chudamani, M.A. (Madras), Hindu College, Tinnevelly, Madras, India
1914			Vivian, Hugh, c/o Messrs. Vivian & Sons, Ltd., Swansea
1884			‖ Voelcker, Edward William, A.R.S.M., F.I.C., Stuart House, 1, Tudor-street, New Bridge-street, E.C.
1884		(C.1891-5, 1902-04)	‖ Voelcker, John Augustus, Hon. M.A. (Cantab.), Ph.D. (Giessen), B.A. and B.Sc. (Lond.), F.I.C., 20, Upper Phillimore-gardens, Kensington, W.
1889			‖ Voss, Walter Arthur, Eastwood-road, Rayleigh, Essex
1885			Vulté, Hermann Theodore, Prof., Ph.D. (Columbia), Teachers' College, Columbia University, New York City, U.S.A.
1901			‖ Wade, Frank, A.R.C.S., F.I.C., 26, St. Ronan's-avenue, Southsea, and Laboratory, H.M. Dockyard, Portsmouth
1903	Trans.		Wadmore, John Mello, M.A. (Oxon.), Aldenham School, near Elstree, Herts.

Date of Election.			
1894			‖Wagner, William George, 12, North Common-road, Ealing, W.
1888			‖Wait, Frank Goodell, Mines Branch, Department of Mines, Ottawa, Canada
1899			Walden, Allan Frederick, M.A. (Oxon.), New College, Oxford
1897			Walford, Samuel Matthew, Wyncote, Hatherlow, Stockport
1909			Waliaschko, Nikolai Awxentiewich, Prof., University Pharmaceutical Laboratory, Sumskaja 41, Charkow, Russia
1881			‖Walker, Archibald, M.A. (Oxon.), F.I.C., Newark Castle, Ayr
1898	Trans.		‖Walker, Andrew Jamieson, Ph.D. (Heidelberg), B.A. (Dub.), 57, Charnwood-street, Derby
1899			Walker, Charles, 802, Culwulla-chambers, 67, Castlereagh-street, Sydney, N.S.W.
1894	Trans.		Walker, Charles Henry Hirst, M.A. (Oxon.), 1, Victoria-terrace, Corkickle, Whitehaven
1889			Walker, Daniel, School of Mines, Ballarat, Victoria, Australia
1911			Walker, Eric Everard, D.Sc. (Lond.), 110, Coggeshall-road, Braintree
1906			Walker, Franklin Wilfred, 42, Hatfield-road, Bedford Park, W.
1912			Walker, George, A.R.S.M., Stonehurst, Lancaster-road, Morecambe, Lancs.
1914			Walker, Henry, 31 and 33, High Holborn, W.C.
1908			Walker, Herbert, Whyttington, Station-road, Wealdstone, N.W.
1890	Trans.	C. 1899-04; V.P. 1909-12	‖Walker, James, Prof., D.Sc. (Edin.), Ph.D. (Leipzig), Hon. LL.D. (St. Andrews), F.R.S., The University, and 5, Wester-Coates-road, Edinburgh
1913			Walker, John Stewart, c/o The Japanese Explosives Co., Ltd., Hiratsuka, Sagami, Japan
1888			Walker, John Thom Ainslie, Marlboro' Inn, Montclair, N.J., U.S.A.
1903			Walker-Pole, Miles, 71, De Korle-street, Braamfontein, Johannesburg, S. Africa
1905			Wall, Francis Henry, 1, Part-street, Southport
1884			‖Wallace, Robert, Prof., The University, Edinburgh
1878			‖Waller, Elwyn, A.M. (Harvard), Ph.D. (Columbia), 7, Franklin-place, Morristown, N.J., U.S.A.
1904			Walling, Léon Edward, 16, Beechhill-road, Eltham, Kent
1910			Wallis, Robert Lauder Mackenzie, B.A. (Cantab.), 2nd Lieut., R.A.M.C., Camp Cottage, Wooburn, Wooburn Green, Bucks.
1902			‖Wallis, Thomas Edward, B.Sc. (Lond.), F.I.C., 5, Hillsboro-avenue, Exeter
1883			‖Walmsley, Robert Mullineux, D.Sc. (Lond.), Northampton Institute, St. John-street, Clerkenwell, E.C. ; and 23, Hilldrop-road, Camden-road, N.

Date of Election.		
1905	Trans.	Walpole, George Stanley, D.Sc. (Melbourne), F.I.C., The Medical Research Committee, The Lister Institute, Chelsea Gardens, S.W.
1888		Walrond, Edward Dalrymple, M.A. (Cantab.), North Eastern County School, Barnard Castle, Durham
1903		Walsh, Thomas Crosbie, c/o Liebig's Extract of Meat Co., Fabrica Colon, Entre Rios, Argentine, S. America
1908		Walton, Sidney Gilbert, Kensington, Thomas-street, Malvern Hill, Croydon, Sydney, N.S.W.
1884		‖Walton, Thomas Utrick, B.Sc. (Glas.), F.I.C., Colonial Sugar Refining Co., Sydney, N.S.W.
1911		Walton, William Keighley, Beechwood, Upper Rushton-road, Thornbury, Bradford
1915		Walworth, George, B.A. (Cantab.), 40, Victor-street, Bradford
1905		Want, William Phillip, 11, Pearfield-road, Forest Hill, S.E.
1916		Ward, Arthur Rokeby, Hazleden Villas, York-street, Wakefield
1864		Ward, George, F.I.C., Buckingham-terrace, Headingley, Leeds
1891		‖Ward, Thomas Armistead, 15, Exchange-street, Blackburn
1907	Proc.	Warner, Charles Horne, B.Sc. (Lond.), F.I.C., 19, St. Dunstan's-road, Barons Court, W.
1871		Warner, George Joseph, Halton Villa, Widnes
1906		Warren, Richard Alfred, Belle Vue, Hallow-road, Worcester
1888		Warrick, Frederic Walmsley, 6, Nile-street, City-road, N.
1895		‖Warrington, Thomas Cotterill, M.A. (Oxon.), 29, Stockwell-street, Leek
1909		Warwick, Guy Ransom, M.A. (Cantab.), c/o Messrs. Carew & Co., Ltd., Distillers, Surat, India
1906		Wasteneys, Hardolph, The Rockefeller Institute for Medical Research, 66th-street and Avenue A, New York City, U.S.A.
1882		Waterfall, Charles James, F.I.C., 4, Queen-square, Bristol
1901		‖Waterhouse, James, Major-General, I.S.C., Hurstmead, High-street, Eltham, Kent
1907		Watkins, Charles Rowlatt, B.A. (Cantab.), Imperial Customs Service, Custom House, Bombay, India
1908		Watkins, Edwin John, 72, King's-road, Peckham, S.E.
1885		‖Watson, Charles, Rose Bank, School-road, Moseley, Birmingham
1913		Watson, Edwin Longstaff, c/o Messrs. David Waldie & Co., Nawabganj, Cawnpore, India
1904	Trans.	Watson, Edwin Roy, Prof., M.A. (Cantab.), D.Sc. (Lond.), c/o Messrs. Thomas Cook & Son, Ludgate Circus, E.C.
1887		‖Watson, Frederick Percy, 6 and 7, Bailgate, Lincoln
1899		Watson, Fred. Sheasby, B.Sc. (Vict.), Albemarle-road, Woodthorpe, Nottingham

Date of Election.		
1906		Watson, Frederick William, B.Sc. (Lond.), F.I.C., Consolidated Gold Fields of South Africa, Ltd., P.O. Box 108, Germiston, Transvaal, S. Africa
1911		Watson, Henry Hough, Braystones, Carnforth
1908	Trans.	Watson, Herbert Edmeston, D.Sc. (Lond.), A.I.C., Indian Institute of Science, Hebbal, Bangalore, India
1906		Watson, John Adam, F.I.C., 80, Oakwood-road, Golder's Green, N.
1883		‖Watson, Thomas Donald, 16, St. Mary's-road, Bayswater, W.
1876	Trans.	‖Watson, William Henry, J.P., Braystones House, Beckermet, Cumberland
1877		Watt, Alexander, F.I.C., c/o Messrs. Macfie and Sons, 34, Moorfields, Liverpool
1904		Watt, Francis Langston, A.R.C.S., F.I.C., City Mart Building, 5, Hamilton-street, Sydney, N.S.W.
1906	Trans.	Watt, Henry Edgar, D.Sc. (Dun.), F.I.C., Blandfield Chemical Works, Wheatfield-road, Edinburgh
1908		Watt, John, Rev. Principal, M.A., and D.D. (Aberd.), 4, Cornwallis-square, Calcutta, India
1908		Watt, Robert Dickie, Prof., M.A. and B.Sc. (Glas.), The University, Sydney, N.S.W.
1883	Trans.	Watts, Francis, C.M.G., D.Sc. (Birm.), F.I.C., Imperial Commissioner of Agriculture for the West Indies, Barbados, West Indies
1872	Trans.	‖Watts, John, M.A. (Oxon.), D.Sc. (Lond.), F.I.C., Merton College, Oxford
1878	Trans.	Watts, John Isaac, Beechfield, Hartford, Cheshire
1888		Way, Edward John, F.I.C., M.Inst.C.E., M.I.M.E., 134–136, Cullinan Buildings, Simmonds-street, Johannesburg, S. Africa
1911		Waygood, Bertie James, 39, Marshall-road, Levenshulme, Manchester
1901		Wayland, William Abraham, 12, Albert-road, St. John's, S.E.
1913		Webb, Edward, D.Sc. (Lond.), Newlyn, Pollard-road, Whetstone, N.
1883	Trans.	Webster, Charles Stuart Stanford, F.I.C., 6, The Quadrant, Redland, Bristol
1909		Webster, John, F.I.C., Laboratory of Pathological Chemistry, St. Mary's Hospital, Paddington, W.
1907		Wechsler, Marcus, D.Sc. (Grenoble), 136, Sinclair-road, Kensington, W.
1904		Weeks, Henry Bridges, F.I.C., The Retreat, Infield-park, Barrow-in-Furness
1908		Weighell, Arthur, 31, The Avenue, Consett, Co. Durham
1898		Weissmüller, Ernest Charles, c/o United Alkali Co., Central Laboratory, Victoria-road, Widnes

Date of Election.		
1909	Trans.	Weizmann, Charles, D.Sc. (Manc.), Ph.D. (Freiburg), 30, Brunswick-road, Withington, Manchester
1913		Welch, Bertie Mandel, 80, Hunter-street, Sydney, N.S.W.
1893		Welchman, Frank Ernest, 25, Upper Park Fields, Putney, S.W.
1891		Wellington, Stephen Newcombe, Assoc.M.I.E.E., 62, London Wall, E.C.
1890		Wells, Sydney Russell, M.D. and B.Sc. (Lond.), M.R.C.S. (Eng.), M.R.C.P. (Lond.), 16, Lower Seymour-street, Portman-square, W.
1897		Welsh, John, M.R.C.S. (Eng.), L.R.C.P. (Lond.), 43, Tarvin-road, Chester
1888	Trans.	Werner, Emil Alphonse, Prof., F.I.C., 1, Fairfield-park, Highfield-road, Rathgar, Dublin
1886		‖Wertheimer, Julius, Prof., D.Sc. (Bristol), B.A. and B.Sc. (Lond.), F.I.C., Merchant Venturers' Technical College, Bristol
1902		West, Joseph, Beechwood, The Avenue, Kidsgrove, Stoke-on-Trent
1909		West, Percy Charles Henry, 61/2, Chancery-lane, W.C.
1916		West, Ralph Winton, 203, Casewick-road, West Norwood, S.E.
1898	Trans.	Weston, Frank Edwin, D.Sc. (Lond.), 29, Sibella-road, Clapham, S.W.
1892		Whalley, Lawrence John de, B.Sc. (Lond.), F.I.C., 18, Brandram-road, Lee, S.E.
1908		Wheatley, William, M.A. (Oxon.), 4, Rock-mount, Adelaide-terrace, Blackburn
1906		Wheaton, Harold Joseph, A.C.G.I., Minster, Walton New-road, Lower Walton, Warrington
1907	Proc.	Wheeler, Edward, A.C.G.I., 117, Main-road, Sidcup, Kent
1902		Wheeler, Edward Jonathan, Ph.D., 79, Chapel-street, Albany, N.Y., U.S.A.
1915		Wheeler, Leonard Richmond, B.Sc. (Lond.), 13, Goda-road, Littlehampton
1909	Trans.	Wheeler, Richard Vernon, D.Sc. (Manc.), Home Office Experimental Station, Eskmeals, Cumberland
1893		‖Wheeler, William Ernest, Rose Towers, Wick-road, St. Anne's Park, Bristol
1911		Wheldon, Alfred Henry Finniss-, Mount Edgecombe Estate, Mount Edgecombe P.O., Natal, S. Africa
1897		While, Arthur James, Armadale, Barrow-in-Furness
1914		White, Alfred John, B.Sc. (Lond.), Hawes Down, West Wickham, Kent
1891		White, Henry, Eastville, Norwood-road, Sheffield
1899		White, Henry Fox, 52, Royal York-crescent, Clifton, Bristol

Date of Election.		
1905		White, John Ledger, D.Sc. (Dun.), 98, Stormont-road, Clapham Common, S.W.; and Battersea Polytechnic, Battersea Park-road, S.W.
1905		White, John William, B.Sc. (Lond.), c/o The E.C. Powder Co., Green Street Green, Dartford
1915		White, Maurice, The Brewery, Romford
1914		White, Norman Cecil, B.A. (Cantab.), B.Sc. (Lond.), 35, Spencer-park, Wandsworth, S.W.
1897		White, Paul Thomas, Hortonfield House, West Drayton, Middlesex
1893		‖White, William Gilchrist, Vicarage View, 133, Tottington-road, Bury
1885		Whitehead, Henry Hammond, 18, Boston-road, Brentford
1896		Whitehead, James, 8, West-street, Rochdale
1901		‖Whitehouse, Philip Lewington, 16, Lombard-street, West Bromwich
1904	Trans.	Whiteley, Charles Edward, 21, Brudenell-view, Leeds
1886	Proc.	‖Whiteley, Richard Lloyd, F.I.C., Municipal Science and Technical School, West Bromwich
1892		Whiteside, John Lowe, 376, St. Helen's-road, Bolton
1863		‖Whitfield, John, 113, Westborough, Scarborough
1899		Whittaker, Christopher Joseph, c/o United Indigo and Chemical Co., Ltd., 1, Cooper-street, Manchester
1889		Whittam, Matthew, M.A. (Cantab.), St. Luke's Vicarage, Thornlaw-road, West Norwood, S.E.
1916		Whitton, William Alexander, B.Sc. (Vict.), The Grammar School, Ross, Herefordshire
1907		Whymper, Robert, A.C.G.I., St. Clare, St. Mary's-road, Ditton Hill, Surrey
1905		Whytehead, Eric Hartwig, c/o Messrs. Brotherton & Co., Ltd., Leeds
1906		Wiffen, Henry John, 17, Albany-road, Manor-park, E.
1889		Wigan, Basil Penwarne, Rhondda Valley Brewery Co., Treherbert, Pontypridd
1905		Wigginton, John Henry Becker, c/o Messrs. Arthur H. Cox & Co., Ltd., Brighton
1896	Proc.	Wigner, John Harrison, Ph.D. (Heidelberg), c/o Messrs. W. Gossage & Sons, Ltd., Soap Works, Widnes
1891		‖Wild, John, B.Sc. (Vict.), A.I.C., Bredbury House, Bredbury, Stockport
1898		‖Wild, William Ernest, B.Sc. (Vict.), 105, Shaw-lane, Dinting, near Glossop
1898		Wilder, Frederick Louis, Morro Velho, Minas Geraes, Brazil
1897	Trans.	Wilderman, Meyer, Ph.D. (Freiburg), B.Sc. (Oxon.), 72, Fellows-road, Hampstead, N.W.

Date of Election.		
1912		Wilkins, Charles Reginald, B.Sc. (Lond.), 8, Crookston-road, Eltham-park, Eltham
1904		Wilkinson, James Alfred, M.A. (Cantab.), South African School of Mines and Technology, P.O. Box 1176, Johannesburg, S. Africa
1903		Wilkinson, James Bates, M.D. and C.M. (Edin.), D.P.H. (Vict.), Town Hall, Oldham
1893		Wilkinson, John, City Gas Offices, 6, George-street, Nottingham
1905		Wilkinson, John Wells, M.A. (Wales and Bristol), Longhope, Essendene-road, Belvedere, Kent
1904	Proc.	Willcox, William Henry, M.D., B.Sc., M.R.C.P. and L.S.A. (Lond.), D.P.H. (Eng.), F.I.C., St. Mary's Hospital, Paddington, W.
1906		Willett, Herbert William Mills, 3, Brasenose House, Kensington High-street, W.
1905		Williams, Alan Herbert, Brockweir, Urmston, Manchester
1913		Williams, Cornelius, B.Sc. (Lond.), A.R.C.S., Central Experiment Farm, Cedara, Natal, S. Africa
1903		Williams, David John, Bath and West of England College of Chemistry and Pharmacy, 6, Cleveland-place, East Bath
1908		Williams, David Thomas, 42, Finsbury-square, E.C.
1895		Williams, Evan, Bradford-road Gas Works, Manchester
1908		Williams, Frederick, M.A. (Oxon.), Bute Villa, Aberdare, S. Wales
1910		Williams, Frederick George, The Gun and Shell Factory, Cossipore, Calcutta, India
1912		Williams, George Mason, 47, Lamb's Conduit-street, W.C.
1909	Proc.	Williams, Herbert Ernest, 22, Heywood-road, Polefield Hall Estate, Prestwich, Manchester
1892		Williams, John, Government Laboratory, British Guiana
1910		Williams, John, B.Sc. (Lond. and N.Z.), 24, Gladstone-street, Belle Knowes, Dunedin, New Zealand
1908		Williams, Joseph Henry, 54, Dongan-road, Wanstead, N.E.
1907	Trans.	Williams, Percy, B.Sc. (Lond.), 94, Telford-avenue, Streatham Hill, S.W.
1883	Proc.	Williams, Rowland, F.I.C., 79, Queen-square, Lancaster
1891		Williams, Seward Whiting, c/o Messrs. Bauer and Black, 25th and Deaborn-streets, Chicago, Ill., U.S.A.
1872	Trans.	‖Williams, Thomas, 15, Heywood-road, Broad-green, Liverpool
1885	Trans.	‖Williams, Walter Collingwood, B.Sc. (Lond.), F.I.C., Public Analyst's Laboratory, 36, Dansic-street, Liverpool
1899	Proc.	Williams, William Arthur, 19, Craylockhart-terrace, Edinburgh
1874	Trans.	‖Williams, William Carleton, B.Sc. (Vict.), F.I.C., Broomgrove, Goring-on-Thames, Reading

Date of Election.		
1915		Williams, Willis John, Essendon, Turner-avenue, Haberfield, *via* Sydney, N.S.W.
1898		Williamson, John Alexander, The Croft, Chase Court-gardens, Enfield, Middlesex
1886	Trans.	Williamson, Sidney, Ph.D. (Munich), F.I.C., c/o The Cooper Research Laboratory, Berkhamsted
1898		Williamson, William, 94, Hainault-road, Leytonstone, N.E.
1896		‖Wills, Sir Edward Chaning, Bart., M.A. (Cantab.), Harcombe, Chudleigh, Devon
1909		Wills, Harry Sampson, 55, Arngask-road, Catford, S.E.
1872		Wills, Joseph Lainson, c/o Otto F. Stifel's Union Brewing Co., Gravois and Michigan-avenues, St. Louis, Mo., U.S.A.
1892	Trans.	Wilsmore, Norman Thomas Mortimer, Prof., D.Sc. (Melbourne), The University, Perth, Western Australia
1885		Wilson, Alfred Charles, F.R.S.E., 118, High-street, Stockton-on-Tees
1879		‖Wilson, Charles Joseph, F.I.C., 14, Suffolk-street, Pall Mall-east, S.W.
1894		Wilson, Christopher, The Grammar School, Manchester
1883	Trans.	‖Wilson, David, M.A. and D.Sc. (Glas.), Carbeth, Killearn, Glasgow
1901		‖Wilson, Duncan Randolph, 7, Sydney-place, S. Kensington, S.W
1913		Wilson, Ernest John, M.A. (Cantab.), F.I.C., Osborne House, Wisbech
1912	Trans.	Wilson, Forsyth James, D.Sc. (Edin.), Ph.D. (Leipzig), Royal Technical College, Glasgow
1908		Wilson, Harry Percy, 223, Maldon-road, Colchester
1875		‖Wilson, James, M.A. (Dub.), Barrister-at-Law, Cotswoldbury, Glengall-road, Woodford Green
1890		Wilson, James Mitchell, M.D. and C.M. (Glas.), D.P.H. (Cantab.), County Hall, Beverley
1895	Proc.	Wilson, John, M.Sc. (Vict.), F.I.C., Battersea Polytechnic, S.W.
1902		Wilson, Lyndon Charles, 5, Wellington-road, Newark-on-Trent
1900	Proc.	‖Wilson, Leonard Philip, F.C.G.I., Rosemont, Holyhead-road, Coventry
1909	Trans.	Wilson, Robert William, 86, Dover-road, South Wanstead, N.E.
1913		Wilson, Siddons Siddons, 4, Northfield-road, East Ham, E.
1871		‖Wilson, William John, c/o Dr. W. M. Watts, Shirley, Vennor-road, Sydenham, S.E.
1884		Wilton, Thomas, The Gas Light and Coke Co., Beckton, North Woolwich, S.E.
1893		Winder, Edward Humphreys, Felton, Ludlow
1894		Wingate, Hamilton More, B.Sc. (Glas. and Melbourne), 28, Temple-grove, Golders Green, N.W.

Date of Election.		
1913		Winstanley, Thomas Harrison, 45, Dicconson-street-west, Wigan
1906		Winther, Christian, Ph.D. (Copenhagen), Ostervold 5, Copenhagen, Denmark
1914		Wintle, Albert Watkins Maggs, 43, Hinton-road, Eastville, Bristol
1898	Trans.	Witham, Ernest, B.A. and B.Sc. (Lond.), The Grammar School, Rotherham
1912	Trans.	Withers, John Charles, Ph.D. (Würzburg), 8, Stanley-gardens, Hampstead, N.W.
1908		Withey, William Henry, B.A. (Cantab.), The National Physical Laboratory, Teddington
1906		Wolfe, Ernest Edwin, Kinsale, Co. Cork, Ireland
1907		Wolff, Mark Arthur, 618, Pacific-building, Vancouver, British Columbia
1902		Womersley, Charles Edward, 151, High-street, Heckmondwike, Yorks.
1889		Wood, Charles, Rossemount, Emm-lane, Heaton, Bradford
1860	Trans.	‖Wood, Charles Henry, F.I.C., Erica, Bournemouth-road, Parkstone, Dorset
1911		Wood, Edward Escott, Hurricane House, Brymbo, Wrexham
1908		Wood, Francis Charles Benjamin, British Vice-Consul, British Consulate-General, Rotterdam, Holland
1902		Wood, Frank Stanley, 12, Carlton-avenue, Hornsea, Hull
1913	Trans.	Wood, Henry, 62, Culverden-road, Balham, S.W.
1913		Wood, Hubert Rogers, c/o Messrs. Fenner and Alder and Co., Ltd., Millwall, E.
1912	Trans.	Wood, John Kerfoot, D.Sc. (Vict.), 304, Blackness-road, Dundee
1898	Trans.	Wood, Thomas Barlow, Prof., M.A. (Cantab.), School of Agriculture, Cambridge
1911		Wood, William, Tyneholme, Dudley-avenue, Roseville, N.S.W.
1903		‖Wood, William Francis John, B.Sc. (Lond.), Ardsley House, near Barnsley
1900		Woodbridge, Walter Bourne, A.C.G.I., c/o A. E. Woodbridge, Esq., The Steyne, Bognor
1871	Trans.	Woodcock, Reginald C., F.I.C., The Sanitas Co., Ltd., Locksley-street, Limehouse, E.
1904		Woodcock, William Henry, Craigfernie, Felbrigge-road, Goodmayes, Essex
1898		Woodhead, Samuel Allinson, M.Sc. (Dun.), F.I.C., Agricultural College, Uckfield, Sussex
1909		Woods, George James, B.Sc. (Lond.), 2, Branksome-road, Merton Park, Merton, S.W.

Date of Election.		
1892		‖ Woods, Hugh, B.A., M.D. and B.Ch. (Dub.), D.P.H. (R.C.P.S.I.), Red House, Bordyke, Tonbridge
1888		Woodward, James, B.A. and B.Sc. (Lond.), F.I.C., Drummond House, 31, Coventry-road, Ilford, Essex
1889		Woolf, Mortimer, Mayfield, Mortimer-road, N.W.
1903		Woolhouse, Sidney Herbert, M.A. and B.Sc. (Dub.), A.R.C.S.I., Eastleigh, Latymer-road, Lower Edmonton, N.
1889		Woosnam, Richard William, F.I.C., Caprons, Hutton, Brentwood
1908	Trans.	Wootton, Hubert Arthur, M.A. (Cantab.), B.Sc. (Lond.), 20, Great College-street, Westminster, S.W.
1903		Worden, Edward Chauncey, M.A. (N.Y.), Milburn, N.J., U.S.A.
1908	Trans.	Worley, Frederick Palliser, Prof., D.Sc. (Lond.), M.A. and M.Sc. (N.Z.), D.I.C., University College, Auckland, New Zealand
1884		‖ Worrall, Jason Hall, F.I.C., Howsley, Chapeltown, Sheffield
1858		‖ Worsley, Philip John, Rodney Lodge, Clifton, Bristol
1906		Wortley, Edward Jocelyn, Director of Agriculture, Paget, Bermuda
1906	Trans.	Wren, Henry, M.A. (Oxon.), D.Sc. (Lond.), Ph.D. (Tübingen), Municipal Technical Institute, Belfast
1905		Wren, William James, A.R.C.S., Seborne College, East London, Cape Colony, S. Africa
1898		Wrench, Charles Arthur, 95A, Southwark-street, S.E.
1908		Wright, Allister MacLean, P.O. Box 617, Christchurch, New Zealand
1908		Wright, Charles Harold, B.A. (Cantab.), F.I.C., Department of Agriculture, Suva, Fiji
1911		Wright, Ernest Walter, 179, Edgware-road, W.
1895		Wright, Harold Edward, c/o Sir B. Samuelson and Co., Ltd., Middlesbrough
1878		‖ Wright, Lewis Thompson, Junior Constitutional Club, Piccadilly, W.; and The Rio Tinto Assay Office, Marsh Gate-lane, Stratford, E.
1894		Wright, Robert, 5, Devonshire-colonnade, Buxton
1911	Trans.	Wright, Robert, M.A. (R.U.I.), Lauriston, Derryvolgie-avenue, Belfast
1914		Wright, Robert James, M.A. (Glasgow), c/o R. Burnett, Esq., 196, Langside-road, Glasgow
1910		Wright, William Norman Stewart, 26, Lansdowne-crescent, Glasgow, W.
1886	Trans.	‖ Wright, William Thomas, 11, Rundle-road, Sheffield
1864		‖ Wrightson, John, Prof., 13, Charleville-mansions, West Kensington, W.

Date of Election			
1906			Wyatt-Edgell, Cecil, M.A. (Oxon.), 87, Merridale-road, Wolverhampton
1884			‖Wyley, William Fitzthomas, Wheatley-street, Coventry
1885	Trans.	C. 1892-6. S. 1893-99, 1903-05 V.-P. 1905-08.	‖Wynne, William Palmer, Prof., D.Sc. (Lond.), F.R.S., F.I.C., A.R.C.S., The University, and 17, Taptonville-road, Sheffield
1913			Wyver, Clifton, Burslem Gas Works, Stoke-on-Trent
1911			Yates, Charles Fursdon, Ronaldene, Witham-road, Isleworth
1908			‖Yates, Harry James, M.I.M.E., Redcroft, Four Oaks, Sutton Coldfield, Birmingham
1908	Trans.		Yates, Joseph, M.Sc. (Manc.), B.Sc. (Lond.), F.I.C., Municipal Technical School, Blackburn
1886	Trans.		Yoshida, Hikorokurō, Prof., Imperial University of Kyoto, Kyoto, Japan
1885			Young, Alfred Collett, 17, Vicar's-hill, Lewisham, S.E.
1903			Young, Andrew, M.A. and D.Sc. (Edin.), Geological Department, South African College, and 32, Rosmead-avenue, Cape Town, S. Africa
1886			‖Young, Brougham, Clarence House, 4 and 8, Arthur-street-west, E.C.
1908	Trans.		Young, Charles Robert, D.Sc. (St. Andrews), B.Sc. (Lond.), The University, Sheffield
1897			Young, Francis Samuel, M.A. (Oxon.), F.I.C., The College, Bishop's Stortford
1877			‖Young, Frank Watson, F.R.S.E., 32, Buckingham-terrace, Botanic-gardens, Glasgow
1890	Trans.		‖Young, George, Ph.D. (Erlangen), F.I.C., Bradda, Church-crescent, Church-end, Finchley, N.
1895			Young, Henry Stow, F.I.C., c/o The Borneo Co., Ltd., Kuching, Sarawak
1894			Young, James, 12, Edge-hill, Plumstead, Kent
1874			Young, John, 164, Bath-street, Glasgow
1910			Young, John, F.I.C., A.R.T.C. (Glas.), 610, Weber-avenue, Akron, Ohio, U.S.A.
1898			‖Young, John Henry, M.Sc. (Vict.), c/o Cassel Cyanide Co., Ltd., Shuna-street, Maryhill, Glasgow
1877			‖Young, John Rymer, The Knoll, Hill Cliffe, Warrington
1882	Trans.	C. 1894-8.	‖Young, Sydney, Prof., D.Sc. (Lond.), B.Sc. (Manc.), Hon. Sc.D. (Dub. and Bristol), F.R.S., F.I.C., Trinity College, Dublin

Date of Election.		
1913		Young, Thomas Howard, P.O. Box 134, Coleman, Alberta, Canada
1873		Young, William Charles, F.I.C., 2, Queen Anne's-grove, Bedford Park, W. ; and Chemical Laboratory, 24, Aldgate, E.
1913	Trans.	Young, William John, D.Sc. (Lond.), M.Sc. (Manc.), Australian Institute of Tropical Medicine, Townsville, N. Queensland, Australia
1910		Yusuf, Syed Muhammad, M.Sc. Tech. (Manc.), c/o Syed Ghulam Imám, Chilkáná, District Saharanpur, U.P., India

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NUMBER OF HONORARY AND FOREIGN MEMBERS ... 21

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BRUNSWICK STREET, STAMFORD STREET, S.E., AND BUNGAY, SUFFOLK.